THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

THE THERMAL DEGRADATION OF POLYMER BLENDS

By

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P R E F A C E.

The work described in this thesis was carried out during the period October 1969 to September 1972 at the University of Glasgow, in the Department of Physical Chemistry, which is under the supervision of Professor G.A. Sim.

I am indebted to the Science Research Council for the award of a Research Studentship, during the tenure of which this work was carried out.

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C O N T E N T S

CHAPTER ONE

INTRODUCTION

A. POLYMER DEGRADATION MECHANISMS

In the field of polymer chemistry, the term degradation may be described as any process leading to physical or chemical change of the polymer structure. Polymer degradation reactions may be induced by a variety of energy-transfer agencies such as heat, light, mechanical impact, supersonic waves and radiation, as well as by chemical attack, and industrially, in the fabrication of commercial materials, a combination of these degradative processes may occur simultaneously. However, for the purpose of making a systematic study of the degradative reactions of polymers as a whole, it is convenient to consider the various separate causes and their general effects. During the last few decades the effect of heat at elevated temperatures on the stability of natural and synthetic polymers has aroused more interest and has been investigated more extensively than that of the other agencies, (1,2).

Thermal degradation has played a significant role in the development of our present knowledge regarding the nature and structure of polymers, both natural and synthetic. One of the classical examples of this approach was Staudinger and Steinhofer's investigation of polystyrene, (3).

The remainder of this chapter will be devoted to the chemical effect of heat on organic polymers of the vinyl type, with the general

structure -- $(CH_2 - CXY)_n$ -- where X and Y can be hydrogen or a or a functional group, since only polymers of this type will be encountered in subsequent chapters of this work.

CLASSIFICATION OF REACTION TYPES

Thermal degradation reactions of polymers have been broadly yet conveniently classified into two groups:- Chain Scission or Depolymerization Reactions and Substituent or Non-Chain Scission Reactions, (1).

Chain scission reactions are characterised by breakdown of the polymer chain backbone, resulting in production of chain fragments. The ultimate products are monomer or substances closely related to it, and the residue retains the chemical characteristics of the parent material, in that monomer units are recognisable in it.

Substituent reactions involve modification or elimination of the substituents attached to the polymer chain backbone, leading to changes in the chemical nature of the repeating unit. The volatile products evolved from such reactions differ chemically from the monomer.

A more detailed discussion of each class is appropriate since both types of reaction will be encountered in later chapters.

CHAIN SCISSION REACTIONS.

Within this group, two extremes of behaviour can be observed. The first is illustrated by polyethylene which, on pyrolysis, yields a broad spectrum of hydro-carbon fragments ranging from C_1 to C_{70}, (2). It has been established that the degradation of this polymer involves random scission of carbon-carbon bonds, producing polymer radicals, which then undergo mutual disproportionation, or hydrogen abstraction reactions. This process continues until the molecules so produced

are of sufficiently low molecular weight to be volatile at the degradation temperature.

The second extreme type of chain scission process can be regarded as a reverse polymerization in which degradation, initiated by homolytic scission, proceeds by an unzipping process to produce large amounts of monomer. Examples of this type of behaviour are provided by poly (methyl methacrylate) and poly (alpha methylstyrene), (4).

Many polymers show intermediate degradation patterns in which appreciable amounts of both monomer and higher chain fragments are formed. These two extremes and all intermediate behaviours may be described in terms of a single free-radical chain reaction, incorporating Initiation, Depropagation, Transfer and Termination, (4) :-

Random Initiation $M_n \xrightarrow{k_i} P^{\cdot}_j + P^{\cdot}_{n-j}$

Terminal Initiation $M_n \xrightarrow{k_i} P^{\cdot}_{n-1} + P^{\cdot}_1$

Depropagation $P^{\cdot}_i \xrightarrow{k_d} P^{\cdot}_{i-1} + M_1$

Transfer $P^{\cdot}_i + M_n \xrightarrow{k_f} M_i + P^{\cdot}_n$

$P^{\cdot}_n \xrightarrow{k_f} P^{\cdot}_j + M_{n-j}$

Termination $P^{\cdot}_i + P^{\cdot}_j \xrightarrow{k_t} M_i + M_j \text{ or } M_{i+j}$

In these equations, $P_i^{\cdot}$, $P_j^{\cdot}$, etc., and M_i , M_j , etc., represent respectively long chain radicals and dead polymer molecules of i, j, etc., monomer units in length.

Using this scheme, the degradation of polyethylene may be explained qualitatively as involving random initiation, followed by transfer, or termination by disproportionation. The low monomer

yield of 1% (2) illustrates the absence of depropagation in the mechanism of decomposition.

Two modes of initiation are believed to occur in poly (methyl methacrylate) (5). The first produces radicals from chain ends, in polymers containing unsaturated end structures. The second, occurring at higher temperatures produces radicals by scission of main chain carbon-carbon bonds. In each case of initiation, the radicals so formed depropagate almost quantitatively to monomer proving that transfer is unimportant.

Thus Simha, Wall and Blatz (6), have shown that while the mechanism outlined generally accounts for depolymerization processes, the range of apparently distinct behaviours is due to differences in the relative importance of depropagation and transfer in different systems. In degradations where depropagation predominates, the molecular weight tends to be maintained, high yields of monomer appear, and the rate decreases throughout the reaction. The effects of transfer on the other hand, are to cause a rapid decrease in molecular weight, the volatile products to contain larger chain fragments with little monomer and for the rate to exhibit a maximum. This theory still accounts for all the principal features of radical depolymerization.

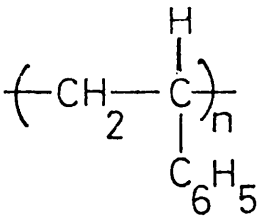
EFFECT OF STRUCTURE ON THE NATURE OF DEPOLYMERIZATION.

In a study of polymer decomposition, the structure of the polymer is of fundamental importance. Thus in the case of depolymerization initiated at chain ends, the initial rate of decomposition will be inversely proportional to the molecular weight of the polymer. In general, observations should be made on the effect of conditions of polymerization, nature of initiator system employed etc., on the subsequent thermal stability of the polymer. In poly (methyl methacrylate), samples prepared using free radical catalysts have

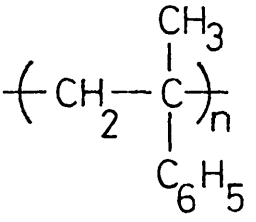
chain ends which are known to be points of initiation for the depolymerization. By contrast, anionically prepared polymer does not possess labile chain ends (5,7).

The nature of thermal decomposition of polymers is determined by competition between depropagation and intermolecular transfer, and this is reflected in the yield of monomer. The occurrence of transfer, either inter or intra, leads to nonmonomreic material and hence reduces the monomer yield. It has been found that a clear relationship exists between the chemical structure of a polymer and the proportion of monomer in the degradation products (4).

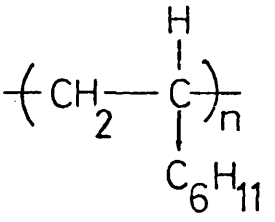
In general, the relative importance of depropagation and transfer depends principally on two factors, namely, the reactivity of the degrading polymer radical and the availability of reactive atoms (usually hydrogen atoms) in the polymer structure (4). Thus transfer is favoured by active radicals and is less likely to take place with resonance-stabilised or sterically hindered radicals, while high monomer yields are obtained from polymers which are devoid of tertiary hydrogen. The effect on the monomer yield is illustrated by the styrene polymers (a) to (c) :-



(a)



(b)



(c)

The monomer yield from polystyrene, (a), is 40% at 300-400°C, while in poly (alpha methyl styrene), (b), it is 100% (4). This may be explained by inhibition of transfer owing to replacement of the tertiary hydrogen atom in polystyrene by an additional methyl group, which also stabilises the first formed radical electronically by an

inductive or hyperconjugative effect. In the case of the hydrogenated polystyrene, (c), where the hydrogen atoms of the cyclohexane ring are more easily extracted than those in polystyrene, the monomer yield is less than 5% (4). The first formed radical from (c) would be expected to be electronically less stable than that from (a), since delocalisation of the unpaired electron by the aromatic nucleus is possible in (a), but not in (c).

SUBSTITUENT REACTIONS.

Among depolymerization reactions there exists the outstanding unifying feature that whatever the detailed mechanism of the breakdown may be, the reaction ultimately resolves itself into progressive breaking of the chain backbone. Substituents can modify these reactions but the essential features of the main chain scission remain.

Substituent reactions, on the other hand, have no comparable unity since they depend entirely upon the chemical nature of the polymer backbone. These reactions will predominate in any given system only if they can be initiated at temperatures lower than that at which main chain bonds are broken, and thus substituent reactions are usually observed at relatively low temperatures. Thermal depolymerization seldom takes place below 200^{o}C even if structural features are most favourable, while substituent reactions, if they take place at all, are frequently quite rapid at this temperature. These reactions, which may compete with or supplant chain scission reactions, can be classified into three main types :-

(a) Elimination Reactions.

(b) Ester Decomposition Reactions.

(c) Cyclisation Reactions.

Elimination reactions, as illustrated by poly (vinyl chloride), involve the elimination of pendant groups as "HX", and the production of conjugated polyene chains :-

$$- CH_2 - CHX - CH_2 - CHX - \longrightarrow - CH = CH - CH = CH - + HX \quad (X = Cl)$$

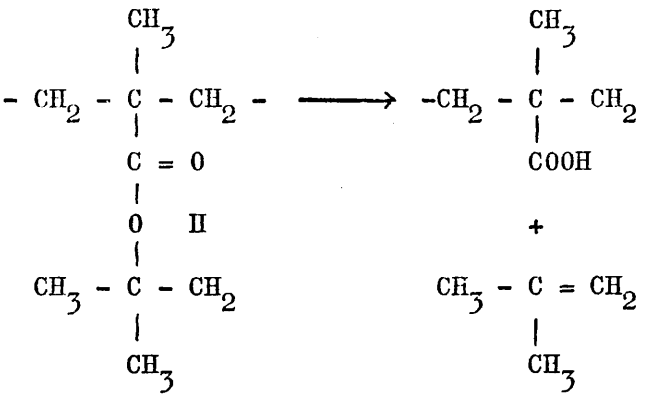
Analogous processes are known for poly (vinyl acetate), poly (vinyl alcohol) and poly (vinyl bromide), where X = CH_3COO, OH and Br respectively.

In poly (vinyl chloride), the mechanism of elimination of HCl has not been clearly elucidated, in spite of extensive study. In a review by Geddes (8), evidence is presented for ionic, molecular and radical dehydrochlorination processes, but in each case it is far from conclusive. There is even insufficient evidence available to permit the selection of one particular structural irregularity as being responsible for the initiation of thermal degradation. These issues, as well as the effect of HCl on the rate of dehydrochlorination will be discussed in more detail in a later chapter.

Poly (vinyl acetate), although slightly more stable than poly (vinyl chloride), degrades in a similar fashion, producing acetic acid and leaving a poly-acetylene residue. In Grassie's reaction scheme (9), the degradation is initiated at chain ends and proceeds through the molecule by allylic activation of adjacent units via a molecular mechanism. Servotte and Desreux (10), while disputing some of Grassie's findings, have shown that a cross-linking process coexists with deacetylation. Again a more detailed discussion of this mechanism will be found in later chapters.

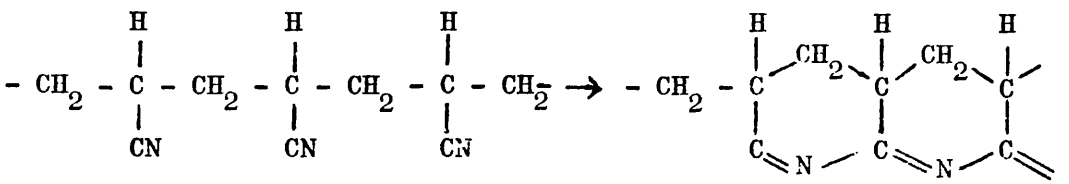
Ester decomposition reactions, involving the production of the parent acid, plus an olefin, have been found in ester polymers, as in short chain esters. When polyacrylates or polymethacrylates decompose in this way the olefinic fragment is liberated as the volatile product, as exemplified by poly (t-butyl methacrylate), which is known to

liberate iso-butene, leaving poly (methacrylic acid) as the first formed product (11) :-



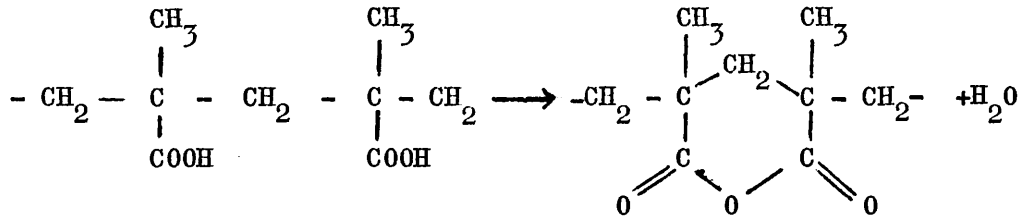
This type of reaction is quite common among esters which have a hydrogen atom attached to the carbon atom B to the ester linkage in the alcohol part of the molecule. Thus while depolymerization to monomer is typical of methacrylate esters, it is the exclusive reaction in poly (methyl methacrylate) which does not have a B hydrogen atom in the alcohol residue. Ester decomposition reactions occur to a greater or lesser extent in other polymethacrylates, with poly (t-butyl methacrylate) representing the other extreme, in that ester decomposition occurs almost to the exclusion of depolymerization. As in the elimination reactions, the residue produced, although polymeric, is unlike the parent material.

In cyclisation reactions, cyclic polymeric structures are obtained by side group rearrangement, with or without concurrent production of volatile products. Thus polyacrylonitrile colours thermally at 175°C due to the linking of nitrile groups to form conjugated carbon-nitrogen sequences (12,13) :-



A similar coloration reaction (and resulting structure) occurs in polymethacrylonitrile (14), although this varies from sample to sample, since the presence of trace impurities can initiate the process.

Poly (methacrylic acid), when heated undergoes a dehydration reaction which results in adjacent six-membered ring anhydrides situated along the polymer chain (15) :-



The mutual interaction of pendant groups may also occur intermolecularly, leading to a cross-linked network.

The wide diversity of substituent reactions does not permit a common reaction mechanism to be written. However, several features common to substituent reactions emerge :-

(a) They lead to products structurally dissimilar to the original polymer.

(b) The final product, (at temperatures above 500°C) is usually a carbonaceous residue, often akin to graphite (16). This is due to the initial formation of cyclic or cross-linked structures which, rather than volatilising completely, may undergo reorientation, and dehydrogenation to give an almost pure carbon.

(c) The formation of conjugated unsaturated structures frequently leads to coloration of the residue.

(d) Substituent reactions often commence at temperatures below those at which depolymerization occurs, and if allowed to proceed to sufficient extents, will also inhibit any potential depolymerization process. This is due to the formation of

structures which do not permit depropagation to pass through them. Such behaviour is found in polymethacylonitrile, where cyclisation occurs at lower temperatures than monomer production (14).

GENERAL CONSIDERATIONS.

The ultimate aim of studies of degradation is the prediction of the thermal stability of a polymer, given its chemical structure. Such detailed predictions are not yet possible, although some generalisations can be made concerning the relationship between structure and thermal stability :-

(a) Polymer molecules often incorporate labile structural abnormalities, at which points degradation may be initiated. Thus unsaturated chain ends can initiate depolymerization in poly (methyl methacrylate); small traces of copolymerised acid greatly reduce the thermal stability of polymethacrylonitrile (17); and the dehydrochlorination of poly (vinyl chloride) is also believed to be initiated at structural irregularities at the chain ends or within the chain itself (8). Thus the Thus the conditions of polymerization, as well as the history of the monomer used, may have a profound influence on the subsequent thermal stability of the polymer.

(b) Many "model" compound reactions may be converted to chain reactions by the polymer environment. Thus dehydrochlorination of poly (vinyl chloride) is not a reaction which would be expected at the temperature where it is encountered, since secondary chlorides do not decompose at temperatures below 350°C (18). As a result, the study of "model" compounds of low molecular weight cannot be expected to elucidate completely the mechanism of degradation of macromolecular analogues.

(c) The mechanisms of degradation of copolymers and of polymer mixtures cannot necessarily be deduced by extrapolation from

from the processes occurring in the homopolymers. For example copolymers of methyl methacrylate and vinyl chloride are less stable than either homopolymer, liberating methyl chloride as a product at temperatures as low as 150°C (19). Mixing poly (vinyl chloride) with poly (methyl methacrylate), on the other hand has pronounced effects on the stability of the latter, and also leads to products not obtained from the degradation of either homopolymer (20, 21).

(d) The formation of discrete ions in decomposing organic polymers is unlikely, since the charge cannot be delocalised by solvation, and the dielectric constant of molten polymers is generally too low to support charge separation. Most polymer degradation mechanisms in bulk are therefore believed to involve uncharged intermediates, occurring via "radical" or "molecular" pathways. Ionic or "ion pair" intermediates may be possible in solution degradation however, or in highly polar polymers.

B. THERMAL DEGRADATION OF POLYMER BLENDS.

In recent years polymer blends have become established materials in the field of commercial plastics, principally because they are easily adapted to specific needs, and can be modified at any time for improvement in one property at a minimum sacrifice of other properties. Polymer blends may be classified (22) as homogeneous systems, which are primarly used to improve processing, and heterogeneous systems, used for imparting toughness. Both systems are used to a lesser extent for reducing the amount of the more expensive material, for introducing thermally reversible crosslinks, and for increasing flame resistance.

The most important of the commercially available polyblends are the impact-resistant styrene and vinyl chloride polymers. The

impact strength of polystyrene is improved in blends with natural or synthetic rubber, and that of poly (vinyl chloride) by blending with butadiene-containing rubbery copolymers, some acrylates, ethylene-(vinyl acetate) copolymers and ABS plastics. This has led to considerable interest in the physical properties of polymer blends, but little attention has been paid to the chemical properties, such as thermal stability. Copolymer decomposition studies have illustrated that the degradation of a polymer molecule can be modified considerably by the presence of a second foreign monomer unit in the chain, and it is therefore of fundamental interest and practical significance to observe the effect of the presence of a second polymer on the degradation of another polymer molecule.

PREVIOUS WORK ON POLYMER BLENDS

Until recently, the most significant study of the degradation of polymer mixtures was that of Richards and Salter (23). These workers found that the thermal degradation of polystyrene could be induced at temperatures at which it is normally stable, by pyrolysis in the presence of poly (alpha-methyl styrene). Poly (alpha methyl styrene) is known to be less stable than polystyrene and as it depolymerises to monomer, it produces radicals which can initiate the degradation of polystyrene by abstracting a hydrogen atom from the polymer chain.

Mizutani (24) has found that the presence of vinyl polymers, such as polystyrene or poly (methyl methacrylate) caused acceleration of polypropylene decomposition. These vinyl polymers also proved effective in forming graft or block copolymers, by interaction of a vinyl polymer radical with the polypropylene chain. Graft copolymers have also been obtained recently by Pavlinec and Kaloforov (25) by degrading polypropylene - poly (vinyl acetate) mixtures.

THERMAL DEGRADATION OF PVC BLENDS.

The degradation of blends containing poly (vinyl chloride) has recently received much attention. Zutty and Welch (19) briefly studied the decomposition of PVC - poly (methyl methacrylate) mixtures as part of an investigation of the corresponding copolymer system. They found that small quantities of methyl chloride were evolved from the mixed system, but did not suggest a mechanism or proceed further with the investigation. Barlow Lehrle and Robb (26), in a comparison of the stabilities of PVC - PMMA blends and VC - MMA copolymers found the former to be more stable, but did not pursue their study.

In a more detailed study of PVC - PMMA mixtures, McNeill and Neil (20,21) found evidence for interaction between the polymers during degradation. PMMA samples, stable to over 250°C when heated alone under programmed heating conditions (10°C/min.), broke down to yield monomer in substantial quantities from 200°C when blended with PVC. This interaction, it was concluded, could best be interpreted in terms of initial chlorine radical attack on the PMMA, which then underwent chain scission and depolymerisation:

(1) $\quad PVC \longrightarrow R\cdot + Cl\cdot$

(2) $\quad Cl\cdot + M_n \longrightarrow RH + P_n\cdot$ $\quad$ Hydrogen Abstraction

(3) $\quad P_n\cdot \longrightarrow P_j\cdot + M_{n-j}$ $\quad$ Chain Scission

(4) $\quad P_j\cdot \longrightarrow P_{j-}\cdot + M_1$ $\quad$ Depropagation.

These mixture experiments, therefore, give a strong indication that the dehydrochlorination of PVC is a radical process. This mechanism also accounts for the delay observed in the production of hydrogen chloride from the mixed samples. If chlorine radicals are chain carriers in a chain reaction for PVC dehydrochlorination, then the removal of even a small number of these radicals may have a significant effect on the dehydrochlorination rate.

Subsequent breakdown of the remaining PMMA in the mixture is shifted to higher temperatures (i.e. stabilised); an interaction which is accounted for by a reaction between methacrylate ester groups and the hydrogen chloride (21). This reaction and mechanism will be discussed in later chapters. The same effect was obtained by Gardner and McNeill (27), by the action of hydrogen chloride from decomposing polychloroprene, on PMMA, during degradation of these blends. However, in this case there was no accelerated breakdown of the PMMA in the early stages, suggesting that the dehydrochlorination of polychloroprene is not a radical chain process.

Retardation of hydrogen chloride production is also shown in blends of PVC with polystyrene and poly (alpha methyl styrene) (28). In the polystyrene blends there is no early production of monomer as in the PMMA blends, but there is considerable subsequent stabilisation of the polystyrene. PVC-poly (alpha methyl styrene) blends give an increased yield of monomer early in the degradation as well as the subsequent stabilisation.

AIM OF THIS WORK.

Results such as those described, clearly indicate that the degradation behaviour of a polymer molecule can be influenced considerably by the presence of a second polymer, although interaction does not occur in every mixed polymer system. Grassie, McNeill and Cooke (29) observed for PMMA - polystyrene blends, that the behaviour of the mixed system was consistent with the view that there was no interaction between the two polymers during degradation.

Since it is not yet possible to predict interactions between macromolecules of different chemical composition during thermal degradation, the primary aim of this work is to study the decomposition of polymer blends, observing any interactions that may occur between

the mixed polymers. Consideration will be given to the species involved; viz. polymers, radicals (both small and macro) and products; and the many possible types of interactions of these species, both with like species and with others.

In the PVC - PMMA blend system, the early initiation of PMMA degradation may be regarded as a test for the production of radicals during the degradation of PVC. This illustrates the second objective of this study, viz. the possible interpretation of interactions as a means of obtaining useful information on the mechanisms of degradation of the homopolymers in the blend.

CHAPTER TWO

APPARATUS AND EXPERIMENTAL DETAILS

POLYMERS USED.

The polymers used in this work came from a wide range of industrial and laboratory sources. Details of preparation (where appropriate), history and characterisation of materials will be given in the appropriate chapters.

THERMAL VOLATILIZATION ANALYSIS.

Although TVA has been the subject of a number of publications (4, 30-34) and is now a well-established technique of thermal analysis, it is desirable, because of the importance of the technique in this work, to give a detailed description of the apparatus and its operation.

PRINCIPLE OF TVA.

The basic objective of TVA is to measure the rate at which volatile material is evolved from a degrading substance over a particular temperature range. When the substance is heated in a continuously evacuated system, a pressure develops as the substance degrades and the volatile products distil from the hot sample zone to a cold trap. This pressure is measured by a Pirani gauge, which is connected to a pen recorder, and a thermogram is traced out, depicting Pirani response as a function of temperature. The heating zone consists of an adapted Perkin Elmer F11 oven and programmer designed for gas chromatography, which can heat the sample isothermally or from ambient temperatures up to 500°C using linear rates of heating, ranging from 1° to 40°C per minute. A

diagram of this basic TVA system is shown in figure (2.1).

The oven arrangement is shown in figure (2.2). The temperature of the oven is measured by a chromel-alumel thermocouple B, placed at the base of the degradation tube, A. This tube, 6 in. in length is constructed from a Pyrex FG 35 flange, with a pyrex glass base. The upper portion of the tube and the greased flange joint is cooled by the water jacket C during the course of an experiment.

DIFFERENTIAL CONDENSATION T.V.A.

The simple TVA system has been elaborated to allow differential condensation of products (33,34). The system is shown in diagrammatic form in figure (23). The principle involved is the same as previously described, Pirani gauge heads being used to register the transfer of volatile degradation products from the heated sample to a liquid nitrogen trap (-196^{o}C). The product stream may pass along four equivalent routes, each with a secondary cold trap, operating usually at four different temperatures, 0^{o} - 45^{o},- 75^{o} and - 100^{o}C respectively. A Pirani gauge is positioned between each of the four secondary traps and the common trap, and a fifth Pirani gauge is positioned after the common liquid nitrogen trap. The responses from the five Pirani gauges are transmitted, via a multi gauge head unit, to a twelve channel recorder where they are recorded in conjunction with the output from the oven thermocouple. Thus volatile products from the sample may be fractionated according to their condensability or non-condensability at each of the five temperatures and a DCTVA thermogram obtained.

Fig. 2.1

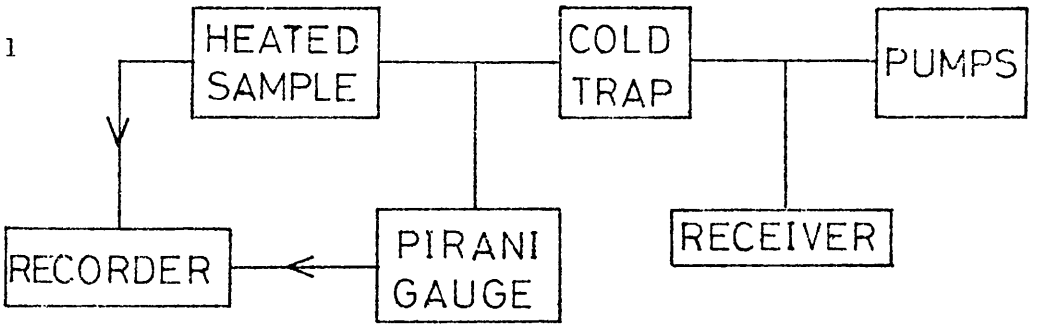
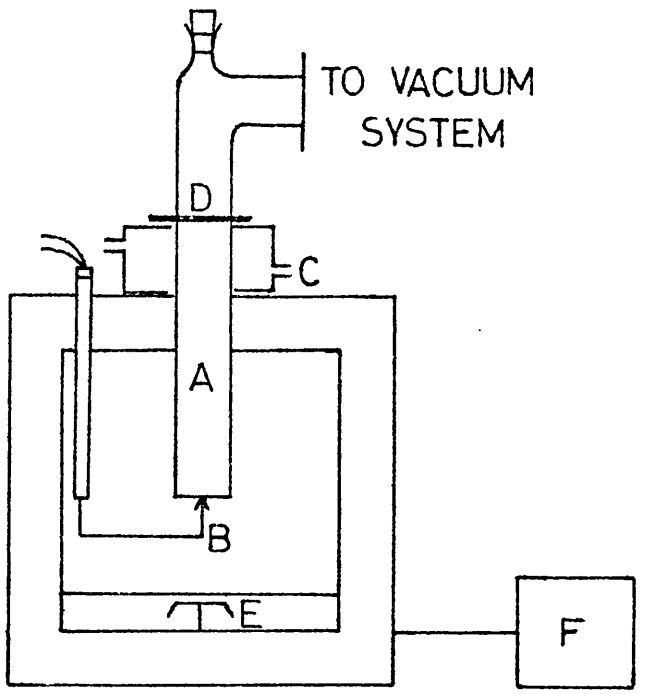


FIGURE (2.1). Schematic layout of basic TVA apparatus.

Fig. 2.2



FIGURE(2.2). Oven Arrangement for TVA.

A, Sample Degradation Tube.
B. Chromel-Alumel Thermocouple
C. Cooling Jacket
D. Removable Flange Joint
E. Oven Fan.
F. Temperature Programmer.

TEMPERATURE CALIBRATION

The temperature recorded during an experiment is that of the fixed oven thermocouple B, shown in figure (2.2), and this is higher than the actual temperature of the interior of the base of the degradation tube. This thermal lag, which is a function of temperature, heating rate, particular degradation tube and position of the oven thermocouple, is caused by the insulating effect of the Pyrex glass, and heat losses from the tube to the cooling jacket. The internal base temperature may be obtained by calibration with a second, internal thermocouple whose junction is surrounded at the point of contact between glass and metal by a small bead of Apiezon "L" grease, to improve thermal contact and to simulate molten polymer (31).

The temperature differential between oven and tube thermocouples is plotted as a function of oven temperature and heating rate in figure (2.4). It can be seen that the thermal lag increases for increasing heating rate and that, surprisingly, it does not increase with increasing temperature, but in fact falls to a plateau in the upper temperature region. McNeill (31) found, that for a particular heating rate, the temperature lag was reproducible over a number of runs and this was confirmed in this work. The large mass of the tube (140g) by comparison with that of the sample, means that the thermal capacity of the tube will be sufficiently great to ensure that thermal effects which may be present during polymer decomposition, have little influence on the sample temperature.

PRODUCT ANALYSIS FROM TVA.

The products arising from degradation of a sample in the TVA apparatus can be classified as volatile products and the involatile residue. The latter may be examined either at the end of an experiment, or at various intervals by interrupting the run. Infra-red or ultra-

Fig 2.3

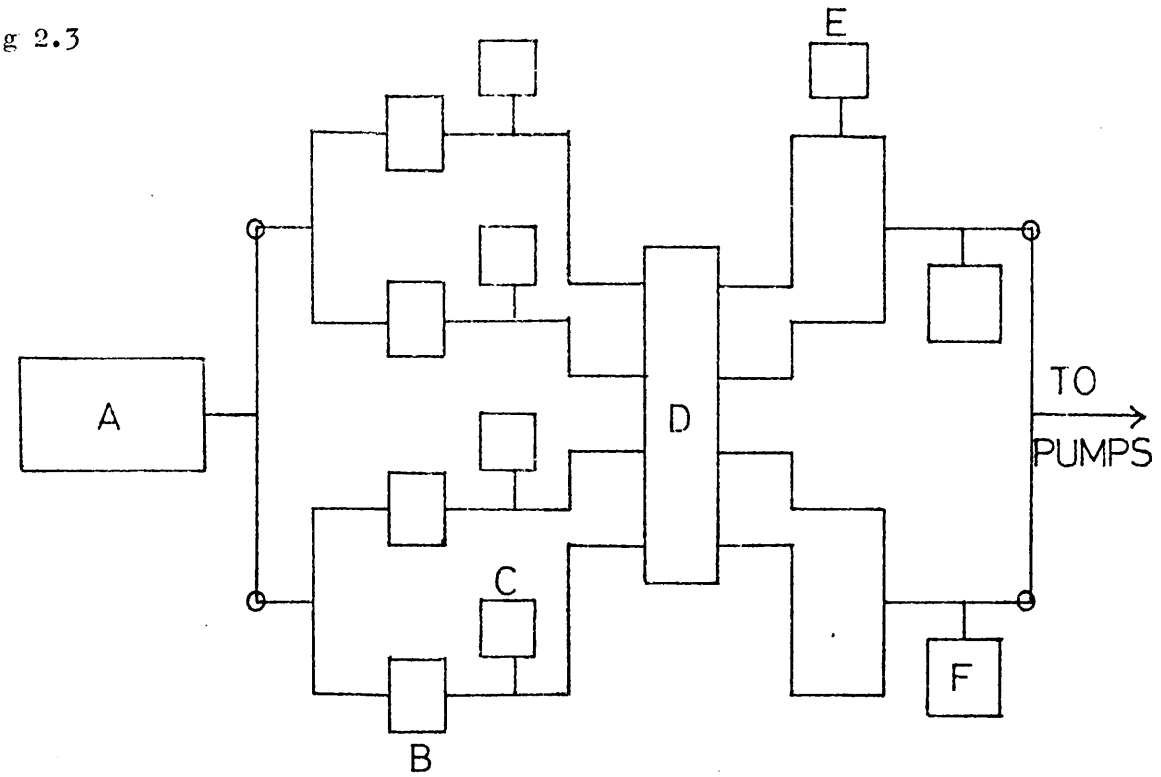


FIGURE (2.3). Differential Condensation TVA apparatus.

A. Heated Sample.
B. Secondary Cold Traps.
C,E. Pirani Gauge Heads.
D. Main Cold Trap.
F. Product Collection Points.

Fig 2.4

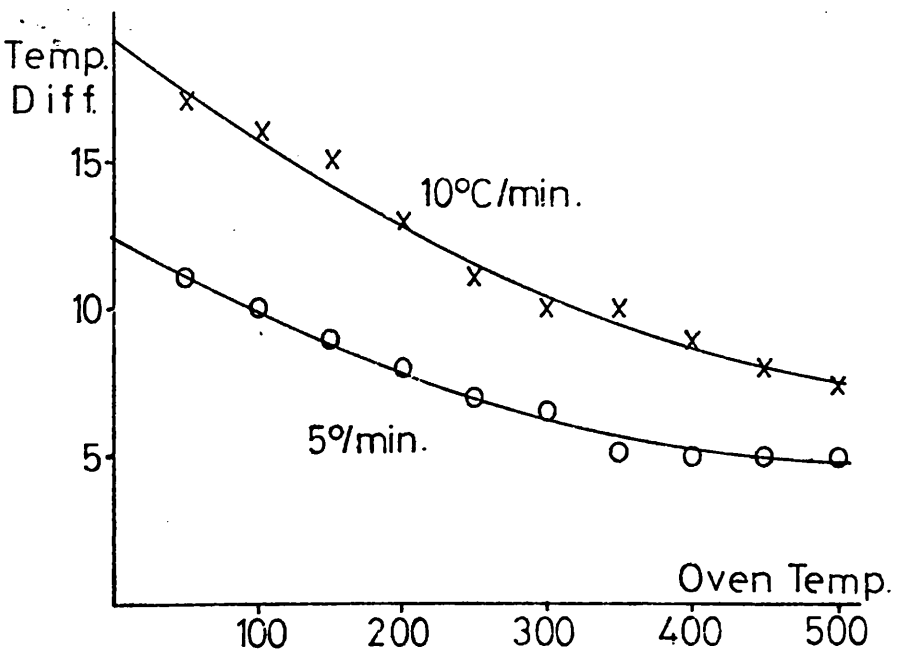


FIGURE (2.4). Temperature Differential Between Oven. Thermocouple and Tube Base.

violet spectroscopy may be applied to determine the nature of the functional groups present and if soluble, the residue can be subjected to molecular weight determinations. The volatile degradation products can be further classified into :-

(a) Those products, volatile at the temperature of degradation, but involatile at room temperature (the Cold Ring Fraction).

(b) Substances volatile at the temperature of degradation, but involatile at the cold trap temperatures (0^{o}, -45^{o}, -75^{o}, -100^{o} and -196^{o}C).

(c) Products volatile even at liquid nitrogen temperature (-196^{o}C).

Products of type (a) collect on the upper portion of the degradation tube, at the area cooled by the cooling jacket C (figure 2.2), and hence the name "cold ring fraction". Analysis may be carried out by wiping this region of the tube with a tissue moistened by solvent, followed by extraction from the tissue, giving a solution of sufficient concentration to permit examination by I.R. or U.V. Products condensed in the cold traps may be isolated and then distilled into a receiver, suitable for subsequent analysis.

There are no means of isolating products non-condensable in liquid nitrogen (e.g. methane, hydrogen and carbon monoxide) which are pumped through the cold trap system under the continuous pumping conditions of TVA. These products can be identified however using an alternative closed vacuum system which incorporates an I.R. gas cell and a cold trap to condense the less volatile substances. A typical system has been described by McNeill and Neil (35).

THERMOGRAVIMETRY.

TG curves were obtained using the Du Pont 950 thermobalance. The boat-shaped platinum sample holder measured 1 x 0.5 x 0.25 cm deep, and the temperature-measuring thermocouple was placed 0.1 cm from the sample holder. For the most part, powdered samples of 10 mg

were degraded to 500°C in a dynamic nitrogen atmosphere (70 ml/min.) at heating rates of 5° or 10°C per min. Isothermal conditions, different atmospheres and samples in the form of films were also employed.

DIFFERENTIAL THERMAL ANALYSIS.

A Du Pont 900 instrument was used to obtain DTA curves. Powdered polymer (10 mg) was packed into a small glass tube 25 mm long by 4 mm diameter, and a chromel-alumel thermocouple was forced down so that the junction pierced the polymer mass. The reference junction was in an identical tube containing small glass beads. Sample and reference tubes fitted into a heater block contained in a glass dome through which nitrogen (or other gases) passed at a flow rate of 1 l./min. Heating was at 10°C/min up to a temperature of 500°C.

INFRA-RED SPECTROSCOPY.

Spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Polymer samples and residues were examined as KBr discs or as films cast from solution on to NaCl plates; cold ring fractions were run in solution (chloroform or carbon tetrachloride). Volatile products were examined as liquids on Na Cl plates or in the gaseous phase.

ULTRA-VIOLET SPECTROSCOPY.

Spectra were obtained on a Unicam SP 800 UV Spectrometer, either in solution, or in the case of polymers, as 20 mg films cast from solution on to the flat base of a silica glass TVA degradation tube, following the method of Gardner and McNeill (36).

MASS SPECTROMETRIC ANALYSIS

This was carried out on volatile degradation products using an AEI MS12 Mass Spectrometer operated at 20 eV. Products collected under vacuum were either directly expanded into the spectrometer or fractionated by condensing the products in cold traps.

MOLECULAR WEIGHT DETERMINATIONS

Number-average molecular weights of polymers were obtained osmotically in toluene solution using a Mechrolab Model 501 osmometer fitted with a Sylvania 300 grade cellophane membrane.

GAS LIQUID CHROMATOGRAPHY.

Two chromatographs were used to obtain both qualitative and quantitative data; the Microtek (G.C.) 2000 R Research Gas Chromatograph equipped with a flame ionization detector, and the Perkin Elmer F 11 Gas Chromatograph equipped with a hot wire analyser. Columns and conditions varied from sample to sample and will be given in the appropriate sections.

For quantitative analysis, the procedure involved adding a known weight of a suitable material as internal standard to a weighed quantity of the liquid sample. Several mixtures of pure samples of each of the products were made up with known amounts of the internal standard and run on the chromatograph to determine the sensitivities of the product compounds relative to the standard. Since the peak area for a particular substance is proportional to the weight present, the peak areas on the GLC traces were measured by planimetry or by the method of weighing "cut-outs". If the sensitivity factor k , for any product Y is defined as the ratio of the peak area of product to standard when equal weights of both are considered, then the percentage by weight of Y in G grams of sample is given by :-

$$\% \ Y = \left(\frac{\text{peak area of Y}}{\text{peak area of standard}} \right) \left(\frac{100}{G / \text{Weight of standard}} \right) \left(\frac{1}{k} \right)$$

STRUCTURE OF POLYMER BLENDS.

In this work interest will be focussed on chemical interactions between polymers in a blend, during thermal degradation. When

chemical reactions are carried out on homopolymers alone, compatibility becomes a significant factor as a result of the difference in structure between the starting material and the reaction product (37). Therefore any explanation of observed interactions in polymer blends must take into account the physical state of the system since unlike macromolecules are, in general, incompatible in the solid state, and under certain conditions in solution also (38, 39).

NATURE OF INCOMPATIBILITY.

Incompatibility manifests itself in solution when unlike polymers present in a common solvent above a limiting total concentration, slowly separate into two layers with a clearly defined phase boundary between them. Analysis of these two layers reveals that one polymer is concentrated in the upper layer, while the other is predominantly in the lower layer. Hughes and Britt (40) interpreted incompatibility in thermodynamic terms as follows ; the mixing process is governed by the relation,

$$\Delta F = \Delta H - T\Delta S$$

where ΔF is the free energy for the mixing and requires to be negative for spontaneous mixing. For mixing of relatively non-polar polymers, ΔS, the entropy factor, is small and positive, since connecting the monomer units by a chemical bond imposes restrictions on the degree of randomness attainable during mixing. Whether ΔF is positive or negative seems to be determined by a balance between ΔH (the heat term resulting from intermolecular interactions) and the $T \Delta S$ term. The small ΔS values make it possible for only a small positive heat term to prevent mixing, and experimentally it is known that polymers, as well as small molecules mix with positive heats of mixing (heat absorbed), so compatibility of macromolecules tends to be the exception rather than the rule.

The phenomenon of incompatibility also occurs in the solid phase, in which polymer blends are prepared by melt mixing, solution blending or latex mixing. The resulting composite is usually opaque or hazy in appearance, owing to the heterogeneity of the mixed system, but if two polymers are compatible, the blend after mixing is transparent rather than opaque (41). Transparency, however, can be present in an incompatible blend if the refractive indices of the two polymers have about the same value or if the particle size of the discrete phase is appreciably smaller than the wavelength of visible light (22). Methods for estimating polymer compatibility include phase separation in solution (38), variation of activation energies (42), viscosity measurements (43, 44) and optical techniques (22). Microscopic methods (especially phase contrast microscopy) have proven extremely useful for studying the structure of heterophase systems, revealing that a mixture of polymers consists of a discrete phase of one polymer dispersed in a continuous phase of the other. The size of the discrete particles or micelles in a polymer blend is frequently in the range of 1 - 15 microns (41).

FACTORS AFFECTING COMPATIBILITY.

(a) Nature of Polymers.

There is no obvious relationship between the compatibility of two polymers and the chemical nature of their monomers. The similarity of the principal chain is not sufficient to ensure the miscibility of the two polymers, nor is the similarity of the substituents. Thus, while blends of polystyrene and poly (ortho methyl styrene) are compatible in solution, blends of ortho and para methyl styrene polymers are not compatible (45). Therefore, while phase separation suggests greater attraction between like than unlike species,

the phenomenon of incompatibility is extremely sensitive to the structure of the polymer chains involved.

(b) Concentration of Polymers.

In mixed solutions of unlike polymers, the phenomenon of phase separation is strongly dependent on the concentration of the solutes. Even where the polymers are incompatible however, the minimum concentration of each polymer required to achieve phase separation varies between approximately 15 to 70 mg/ml, depending on the solvent (46).

(c) Molecular Weight of Polymers.

Since the incompatibility of unlike polymers is a consequence of the molecular size, it is not unexpected that molecular weight should be an important factor in phase separation. The effects of molecular weight are manifested in two different ways;- (i) there is a more complete separation of phases for higher molecular weight material, and (ii) the limiting minimum concentration of solute for phase separation decreases with increasing molecular weight (45).

(d) Temperature.

Temperature affects phase separation only slightly and has not been investigated thoroughly, but it has been observed that the rate of separation into two phases is greater the lower the temperature (38).

CONSEQUENCES OF INCOMPATIBILITY.

Up to the present time, no way has been found to overcome the mutual incompatibility of unlike polymer molecules. Thus any polymer blend will not form a true mixture, and certainly not a solid solution. In the solid state, domains, or micelles of one polymer will be distributed throughout the matrix of the second polymer and any chemical interaction which takes place between the components in such a system must either occur at phase boundaries, or involve the diffusion

of a species formed in one phase into the second phase. In polystyrene - poly (alpha methyl styrene) blends, Richards and Salter (23) postulated a heterogeneous system, consisting of micelles of poly (alpha methyl styrene) in a matrix of polystyrene. These workers suggested that the initiation of polystyrene degradation is caused by diffusion into the polystyrene matrix, of monomer radicals produced by degradation of poly (alpha methyl styrene) within the micelles. The diffusion of these monomer radicals Richards and Salter believed, should have about the same diffusion constant as the monomer, and thus should occur in preference to diffusion of the first formed macromolecular radicals.

However, the interaction of a polymer radical with a polymer molecule of another type cannot be ruled out, since Mizutani (24) has shown that block and graft copolymers were formed during degradation of poly propylene - vinyl polymer blends. Pavlinec (25), in the degradation of poly propylene-poly (vinyl acetate) mixtures, obtained graft copolymers at the beginning of the degradation only. However, it was suggested that the increasing density of the polymer network of partially deacetylated poly (vinyl acetate) was likely to accelerate phase separation within the system, and so interfere seriously with the formation of interpolymer during thermal degradation.

REPRODUCIBILITY OF SAMPLE FORM.

The most serious consequence of the heterogeneity of polymer blends is the difficulty of achieving reproducible sample form in different experiments. For a valid comparison to be made, one polymer should be dispersed to the same extent in the other polymer on each occasion. The ultimate test of any procedure for preparing the blend will be the reproducibility of the subsequent degradation experiments.

Richards and Salter (23) pyrolysed blends obtained by freeze-drying a solution of the two polymers in benzene. Mizutani's method (24) involved either, evaporating to dryness, under continuous stirring, a slurry made from polypropylene dispersed in a solution of the second polymer, or precipitation of the slurry in methanol. Pavlinec (25) prepared his mixtures of polypropylene and poly (vinyl acetate) by intensive stirring in air at 105°C for up to 20-25 minutes. For the most part, the technique of preparing polymer mixtures for this work was that originated by Grassie, McNeill and Cooke (29), and developed by McNeill and Neil (20). This method involved studying the mixed and unmixed samples as films, prepared by evaporation of a solution of the polymers in a common solvent.

COMPARISON OF MIXED AND UNMIXED SYSTEMS.

In any study of the degradation of mixed polymer systems, a method must be found for comparing mixed and unmixed systems of the polymer pair, under similar conditions. One approach to this problem used by Grassie, McNeill and Cooke (29), is to obtain TVA curves for known weights of the component polymers, and for the same weights of the polymers in the form of a mixture; and then to determine whether the behaviour of the latter is consistent with what would be expected by simply "adding" the TVA curves for the individual polymers. The non-linearity of the Pirani gauge response (32), and the different response towards similar amounts of different substances, however, limits the value of this approach. A more convenient technique described by McNeill and Neil (20), involving fewer experiments, was adopted. This method involved degrading known weights of the two polymers simultaneously, but in an unmixed condition, and comparing the results of those obtained using the same experimental arrangement, but with mixed samples.

The experimental procedure involved the use of a twin-limbed

degradation tube, with a flat base to each limb, described by McNeill and Neil (20) and depicted in Figure(2.5). Known weights of each polymer were placed in the separate limbs of the tube and a normal TVA experiment carried out. The experiment was then repeated with equal weights of the polymer blend in each limb of the tube, such that the total weight of each polymer was the same in each case. Thus a comparison could be made, under the same conditions, of the behaviour of the two polymers degraded separately, and as a blend. Care was taken that the degradation tubes were inserted in the oven in such a way that the samples were always in the same position in the oven.

METHOD OF PREPARING SAMPLES FOR DEGRADATION.

Film preparation was the same as that of McNeill and Neil (20). Solutions of the two polymers under study, of known concentration (20 mg/ml), were made up in a common solvent purified, if necessary, before use. A mixed solution of the two polymers was then obtained by combining suitable volumes of the two solutions and shaking thoroughly. At the concentrations used in this work (never greater than 20 mg/ml), phase separation was not observed in the mixed solutions, even when they were left to stand for periods of several weeks. For the study of the unmixed polymers, equal volumes of the two solutions were placed in separate limbs of the twin-limbed degradation tube and the solvent removed by continuous pumping in a vacuum oven at ambient temperature. For the mixed polymer systems, the same tube or tubes were used. The mixed polymer solution was shaken thoroughly, equal volumes were placed in the two limbs, and the polymer films made as before.

Often the polymer films were opaque or only slightly transparent but they were continuous and even, as were the residues

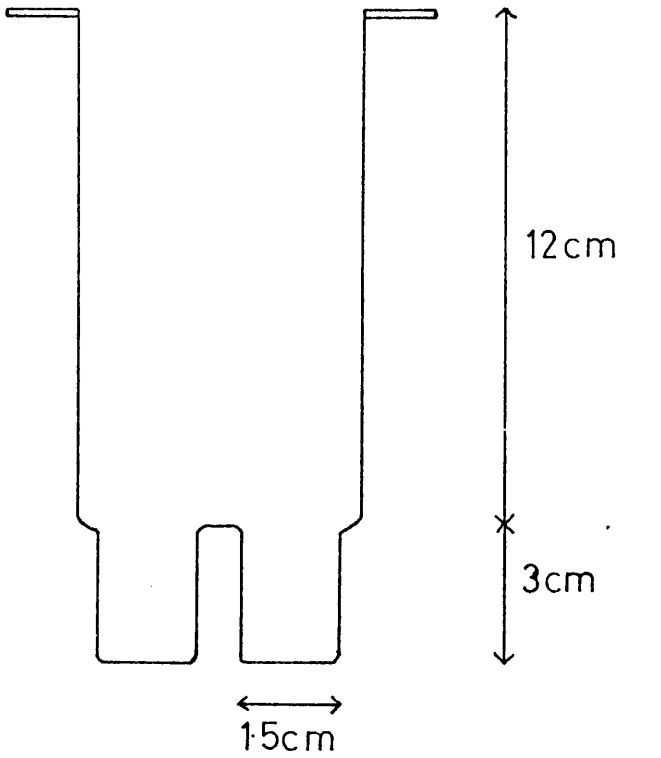


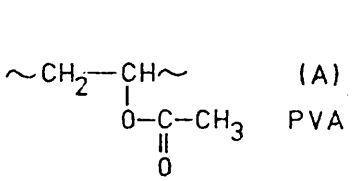
FIGURE (2.5). Sample Tube for Study of Polymer Blends by TVA.

from degradation. Furthermore, the TVA curves for the mixed samples were reproducible and hence the experimental conditions were considered to be satisfactory for the study of polymer blends.

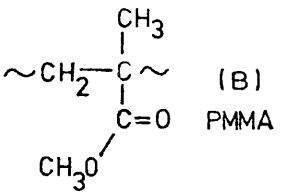
CHAPTER THREE

THE THERMAL DEGRADATION OF POLY (VINYL ACETATE) - POLY(METHYL METHACRYLATE) BLENDS.

The thermal degradation of poly(vinyl acetate), (A) and poly (methyl methacrylate), (B), was discussed in chapter one.



(A) PVA



(B) PMMA

The decomposition of poly (vinyl chloride) - PMMA mixtures was also described, illustrating the interactions which take place when mixtures of these polymers were degraded and how this information was used to elucidate the mechanism of dehydrochlorination of PVC. The mixed polymer system, PVA - PMMA provides an analogous situation because of the similar degradation behaviour of PVA and PVC, and thus it may be possible to use information from any observed interactions to resolve the mechanism of deacetylation of PVA.

INTRODUCTION.

Grassie's basic observations of the deacetylation of PVA, (9) have been substantiated by other workers, viz. loss of acetic acid proceeding along the polymer molecule by a chain mechanism, leaving a conjugated, highly coloured polyene residue. The reaction scheme proposed by Grassie involves initiation at chain ends, and propagation along the polymer molecule by allylic activation of adjacent acetate units via a molecular mechanism: termination occurs when the reaction has proceeded to the end of a chain or to some point of structural imperfection that blocks further acetic acid formation. This scheme may be represented by the following sequence:-

$$Q \xrightarrow{k_1} D_1 + A$$

$$D_n \xrightarrow{k_2} D_{n+1} + A \qquad n \geq 1$$

Here, a chain molecule, Q, is transformed into a chain, D_1, with one double bond and an acetic acid molecule, A, is evolved. Subsequent A's, are much more easily removed from the chains ($k_2 > k_1$).

At the beginning of the reaction,

$$\sum D_n = k_1 Q\, t$$

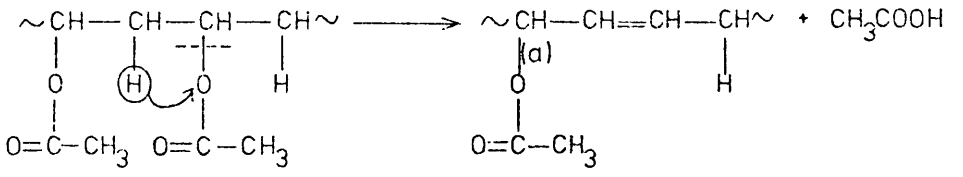
$$\frac{d(A)}{dt} = k_2 \sum D_n + k_1 Q \approx k_1 k_2 Q\, t$$

and hence

$$2A = k_1 k_2 Q\, t^2.$$

Grassie (9) obtained straight lines for $\frac{d(A)}{dt}$ in the early stages of reaction. Also, acid production gave a linear relationship with reciprocal molecular weight of sample, thus leading Grassie to conclude that initiation takes place at chain ends.

The work of Servotte and Desreux (10), while substantiating Grassie's basic observations, differed on several important points. Firstly, these workers obtained absolute rate values three times smaller than Grassie's; secondly, the rate of deacetylation was found to be independent of molecular weight; and thirdly the existence of a cross-linking reaction was observed. Madorsky (2) has suggested that deacetylation can be explained by thermal scission of C - O bonds, as the initiation step, occurring randomly along the chain. The C - O bonds are weaker than the C - C bonds so that, when the polymer is heated, these bonds break first, and this process is accompanied by abstraction of hydrogen from an adjacent carbon to form acetic acid and a double bond in the chain.



Since the C - O bond (a) is now in the β - position to a double bond in the polymer molecule, it breaks more easily than the other C - O bonds in the chain and formation of acetic acid thus proceeds as a chain reaction. In some cases, abstraction of a hydrogen atom by an acetate free-radical may take place inter-molecularly, from other chains, thus resulting in cross-linkages.

Pavlinec and Kaloforov (25) consider the observed rapid cross-linking of PVA as surprising, if initiation of deacetylation at chain ends only, is assumed. These workers have postulated that all the acetate groups have the same reactivity, leading to random loss of acetic acid along the polymer chain. The existence of a conjugated polyene residue has been confirmed by ultra-violet spectroscopy studies of the degraded polymer residue. Gardner and McNeill (36) found six or more double bonds in conjugation, less than for degraded PVC, while Zimmermann (47) detected polyenes with up to twelve conjugated double bonds in discoloured PVA.

One other point of the thermal degradation of PVA deserves mention, and that is the production of small amounts of volatile products, other than acetic acid. Grassie (9) found that, while acetic acid accounted for up to 95% of the evolved volatiles, about 5% consisted of carbon dioxide, water and ketene, all of which, it was suggested, arise from acetic acid decomposition. Servotte and Desreux (10) did not observe carbon dioxide or ketene, but Gardner and McNeill (36) have observed by TVA and infra-red spectroscopy, carbon dioxide, ketene, carbon monoxide and methane (besides acetic acid) although

no deductions were made on possible mechanisms of formation.

Therefore, although the overall reaction has been clearly formulated, the detailed mechanism of PVA degradation has not been fully elucidated.

Many of the above points are illustrated most concisely in the TVA trace for PVA, and it is appropriate at this point to introduce TVA with reference to PVA and PMMA, the two polymers used in this blend system. Figure(3.1) illustrates the TVA behaviour for PVA (B.D.H.) and also incorporates the key to the traces for the different trap temperatures. This diagrammatic representation will be used for TVA traces throughout this work.

The large peak with rate maximum around 320°C in this trace, corresponds to deacetylation, producing acetic acid. However, during the elimination reaction, there are evolved, products non-condensable at -75°, - 100° and - 196°C, indicated by concurrent response from the Pirani gauges situated after these cold traps. The Pirani gauge after the 0°C trap corresponds to all volatile products, while the gauge after the -196°C trap responds only to the non-condensable gases, methane and carbon monoxide. The differences in Pirani response, between the -75° and the -196°C traces, have been interpreted as being due to the presence of water, carbon dioxide and ketene (36). All of these substances (except water) have been identified by infra-red analysis of gaseous products. Acetic acid is completely trapped at the three lowest temperatures, but at -45°C, it condenses and distills over to the liquid nitrogen trap at a steady rate, causing the - 45°C trace to stay at a constant height above the -75°C trace. This is known as the Limiting Rate behaviour (34).

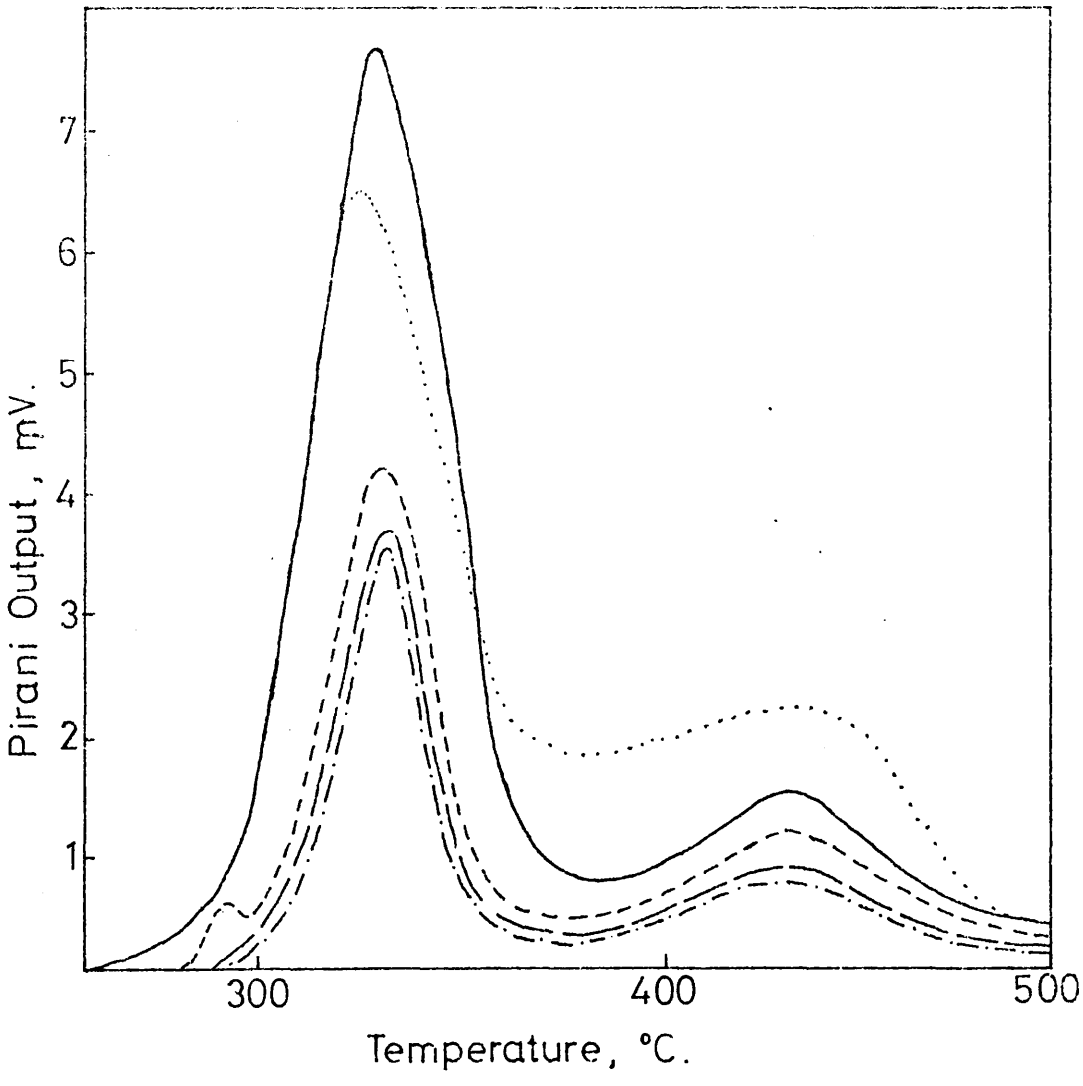


Figure (3.1). TVA Curve for PVA (BDH). Sample as 50 mg film. Heating Rate 10°C/min.

KEY.

——————— 0° Trace.

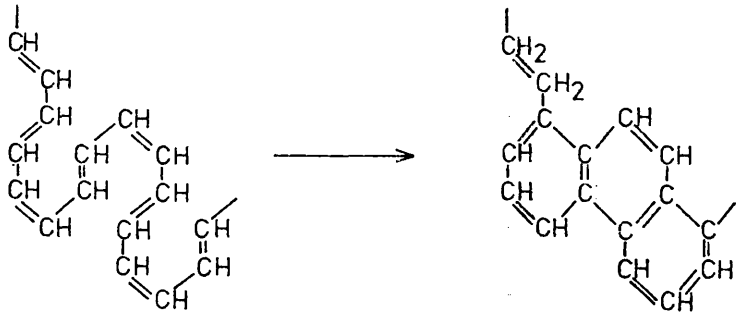
..... -45° "

- - - - - - - - -75° "

——— — — -100° "

—·—·—·— -196° "

The high temperature peak above 400°C results from products, a large proportion of which, are non-condensable at -196°C, and which are formed by break-up of the unsaturated polyene chains. Also occurring at these higher temperatures is the formation of aromatic rings from the conjugated olefinic chains by a Diels-Alder mechanism, either inter- or intra-molecularly.



It is thought that this reaction does not proceed simply by elimination of hydrogen, but by hydrogen transfer to an adjacent unsaturated group (48, 49).

The thermal degradation of PMMA has been shown to give almost quantitative yields of monomer (4,5). TVA curves for this polymer shown in figures (3.2) and (3.3), show the typical behaviour of a single substance giving a limiting rate in the -75°C line. The principal peak and shoulder of figure (3.2) correspond to monomer production by the two different mechanisms of initiation; the shoulder being due to depolymerization initiated at unsaturated chain ends and the principal peak to initiation of depolymerization by random chain scission. McNeill (7) has shown that the first peak is greater, and the second peak correspondingly reduced for samples of lower molecular weight. The sample of PMMA shown in figure (3.2) is of high molecular weight (> 2,000,000) and thus has a first peak, for chain end initiated depolymerization, which is small compared with the second peak for initiation by random chain scission. As the molecular weight of samples decreases, the first peak becomes greater, but with high molecular weight polymers

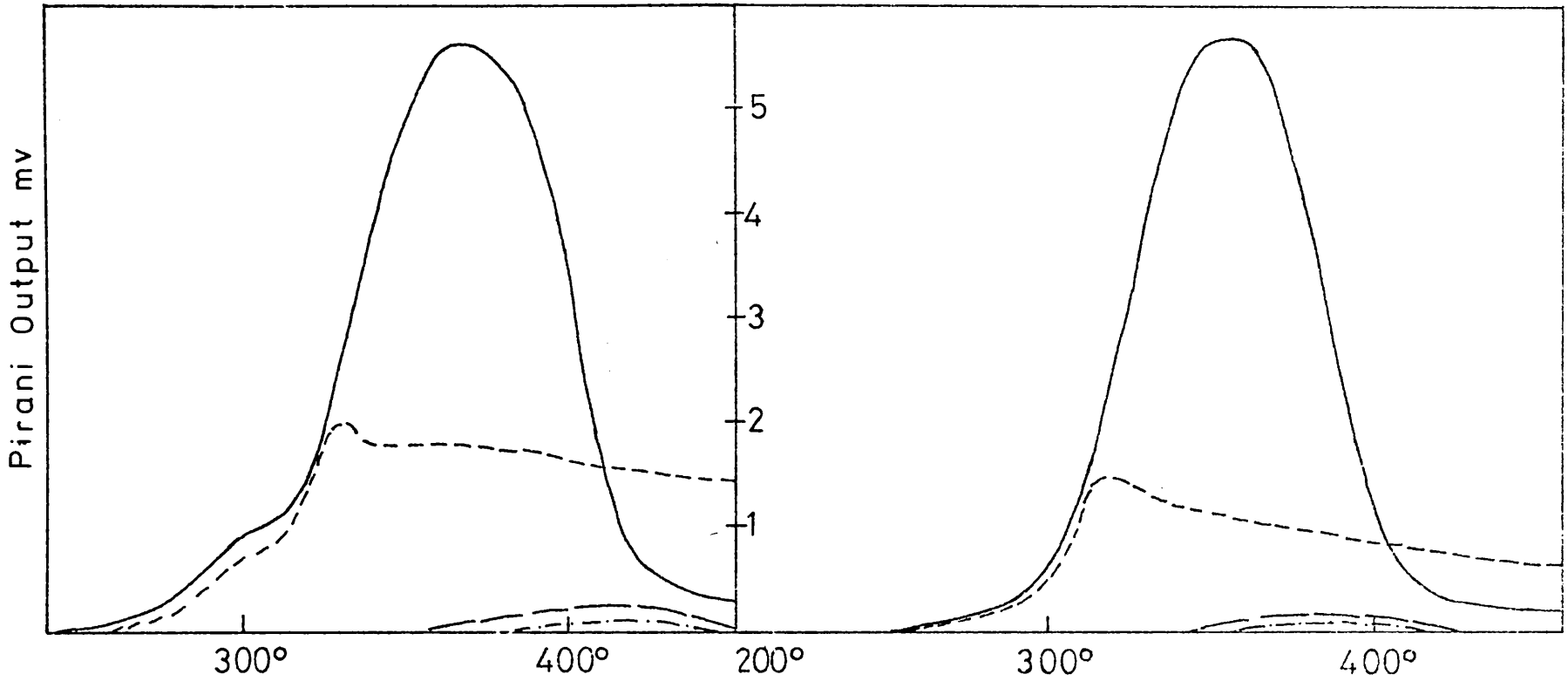


FIGURE (3.2) TVA Curve for PMMA (R1).
Sample as 50 mg. Film.
Heating Rate 10°C/min.

FIGURE (3.3) TVA Curve for PMMA (An 2).
Sample as 50 mg Film
Heating Rate 10°C/min.

(> 500,000), it appears merely as a shoulder on the second peak. In PMMA samples prepared by an anionic mechanism, there are no unsaturated chain ends in the molecules, and hence there is no peak for monomer production initiated at unsaturated chain ends, and only one peak for random scission initiated depolymerization appears in the TVA traces, as shown in figure (3.3).

PREPARATION OF POLYMERS.

Six polymer samples were studied, so that the effects of small changes in structure on the degradation of the blends could be observed. Table (3.1). lists the polymers used in this work, brief details of their history and number-average molecular weights.

Anionic PMMA (PMMA An2) was prepared according to the method of Overberger (50). Methyl methacrylate monomer was washed with sodium hydroxide ($^{N}/_{100}$) to remove inhibitor, distilled under vacuum, and dried over calcium hydride. The polymerization was carried out in toluene solution, under a dynamic nitrogen gas flow at $0^{o}C$. Beforehand, nitrogen had been blown through the toluene to remove oxygen. The reaction was effected by slowly adding the monomer to the catalyst (Phenyl magnesium bromide) in toluene solution. The polymer was isolated by precipitation in petroleum ether and washed with water containing 20% methanol. After reprecipitation in methanol from toluene solution, it was dried under vacuum at $40^{o}C$ for several days. The same purification procedure was employed for the other PMMA samples, while the PVA samples were purified by precipitation in petroleum ether from benzene solution and dried in the same manner as for the PMMA samples.

TABLE (3.1)

POLYMER SAMPLES

Polymer	Mn	History
PVA (BDH)	37,100	B.D.H. sample purified by reprecipitation.
PVA I	301,000	Bulk polymerization at 50°C using benzoyl peroxide (.025%).
PVA II	356,000	Bulk polymerization at 50°C using azodiisobutyronitrile (.025%).
PMMA R1	2,000,000	Bulk polymerization at 60°C using azodiisobutyronitrile (.01%)
PMMA R2	675,000	Bulk polymerization at 60°C using azodiisobutyronitrile (.05%).
PMMA An2	150,000	Prepared by anionic initiator. See text.

RESULTS AND DISCUSSION.

DEGRADATION BY TVA.

Samples were examined as films cast from mixed and unmixed solutions of the polymers in benzene, acetone and cyclohexanone. The sample size of each polymer was 20 mg, or fractions of 20 mg in experiments involving various ratios of the polymers. The heating rate employed in these experiments was 10°C/min. unless stated otherwise.

As described in chapter one for mixtures of PVC and PMMA, it was found convenient to compare the behaviour of the blends by TVA, with the composite TVA curve obtained from simultaneous degradation of the two homopolymers in the unmixed condition. The situation in the

PVA - PMMA system is more complex for two reasons. Firstly, interpretation of TVA traces and hence product identification from TVA is difficult owing to the more complex pattern of PVA volatilization compared to that for PVC, which eliminates only hydrogen chloride in the first stage of degradation. Secondly, the greater thermal stability of PVA compared with PVC is reflected in partial overlapping of the peaks for PVA and PMMA in the TVA traces. However, it is possible to observe differences in the TVA behaviour of mixed and unmixed samples of PVA and PMMA.

TVA traces for equal amounts of PVA and PMMA, examined as mixed and unmixed systems are shown in figure (3.4). The TVA trace for the unmixed system illustrates the overlapping of the volatilization peaks of both polymers. The PVA peak, with concurrent production of products non-condensable at -75^{o}, $-100^{o}C$ and $-196^{o}C$, occurs at lower temperatures than the PMMA peak which appears almost as a shoulder on the PVA peak. The limiting rate at $-75^{o}C$, due to methyl methacrylate monomer is clearly apparent however.

There are several differences between the mixed trace and the unmixed trace. These include slightly earlier initiation of volatilization; a small increase in the peak height of the first peak; a delay in production of the non-condensable products associated with the PVA peak; the PMMA peak becoming a definite peak at higher temperatures and being reduced in height; and an increase in the production of material non-condensable at -100^{o} and $-196^{o}C$, at higher temperatures (in excess of $400^{o}C$) in the TVA trace. Comparing with the observations of PVC-PMMA TVAs (20), the slight increase in peak height may indicate that initially there is an increase in methacrylate monomer production and a corresponding delay in acetic acid production. This latter point is reasonable

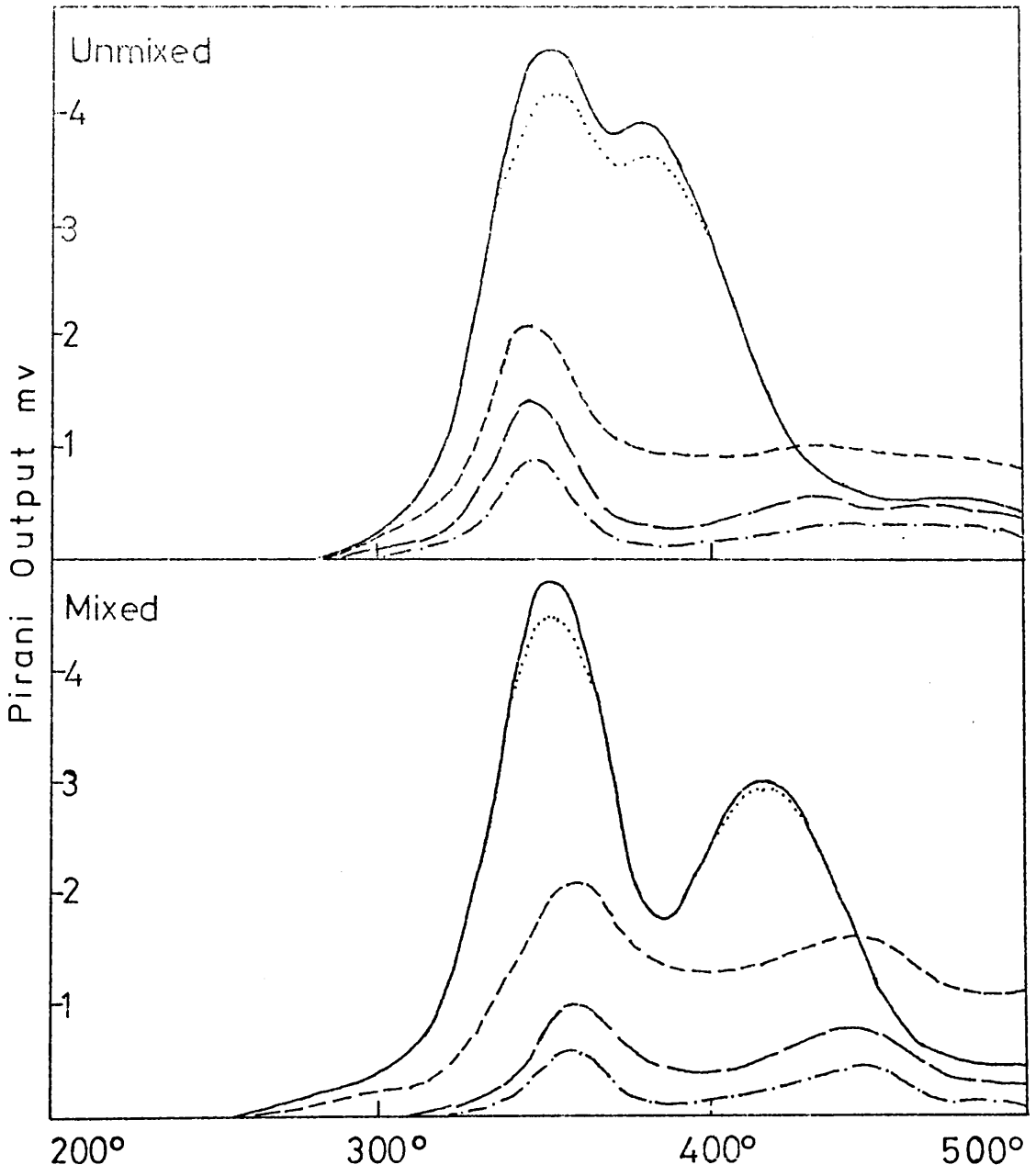


FIGURE (3.4). TVA curves for equal amounts of PMMA (Ri) and PVA (BDH), (20 mg of each polymer), degraded as unmixed and mixed films.

if it is assumed that production of non-condensables from PVA is concurrent with deacetylation. A similar effect has been shown for (vinyl acetate) - ethylene copolymers, in which a delay in non-condensable production is concurrent with the delay in acetic acid production (chapter six) and thus this assumption appears valid. McNeill and Neil (20) interpreted the delay in PMMA breakdown and production of highly volatile material which occur at higher temperatures as the result of stabilization of the PMMA. All of these points were found to be reproducable in TVAs of films cast from the three different solvent systems, benzene, acetone and cyclohexanone, and also in TVAs using the different polymer samples.

Figures (3.5) and (3.6) illustrate the effect of varying the ratio of PMMA to PVA ($^{5}/_{1}$ and $^{10}/_{1}$ by weight of PMMA to PVA respectively). The interactions occurring in the mixed samples may be observed clearly in these diagrams, viz. the increased volatilization in the early stages of degradation, and the subsequent stabilization of PMMA breakdown shown by a movement of the temperature of maximum volatilization rate (Tmax) to higher temperatures and production of non-condensable material above 400°C. It is more difficult to predict accurately the behaviour of acetic acid production because of the small sample sizes of PVA used in these degradation experiments.

Reducing the heating rate from 10°C/min. to 5°C/min does not significantly affect the pattern established from the preceeding TVA traces. The interactions observed in the mixed system shown in figure (3.7) are qualitatively the same as those observed from TVA traces obtained at a heating rate of 10°C/min.

At this stage it is convenient to summarise the observations from the TVA experiments.

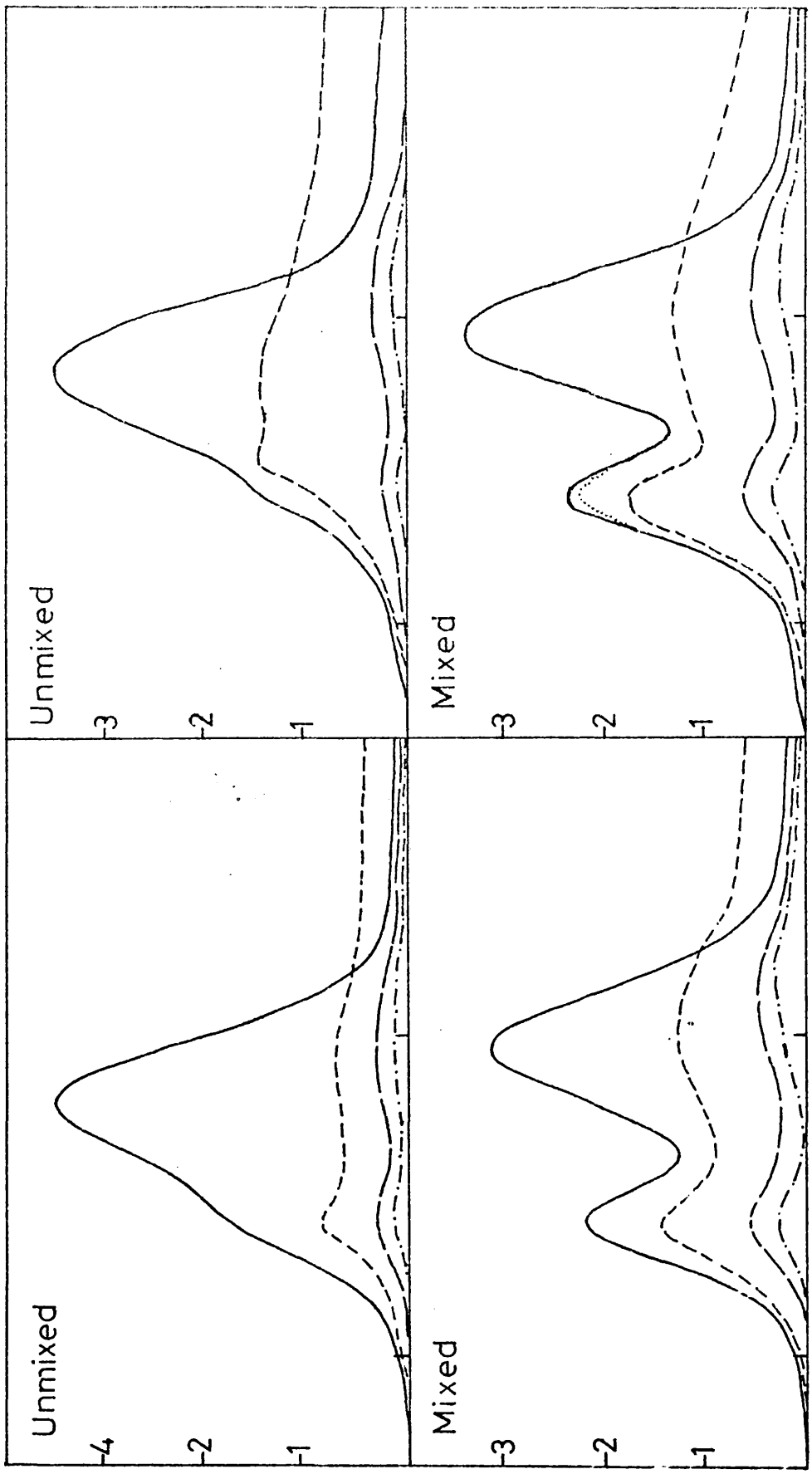


FIGURE (3.5). TVA curves for 20 mg PMMA (An2) and 4mg PVA (BDH), degraded as unmixed and mixed films.

FIGURE (3.6). TVA curves for 20 mg PMMA (An2) and 2 mg PVA (BDH). degraded as unmixed and mixed films.

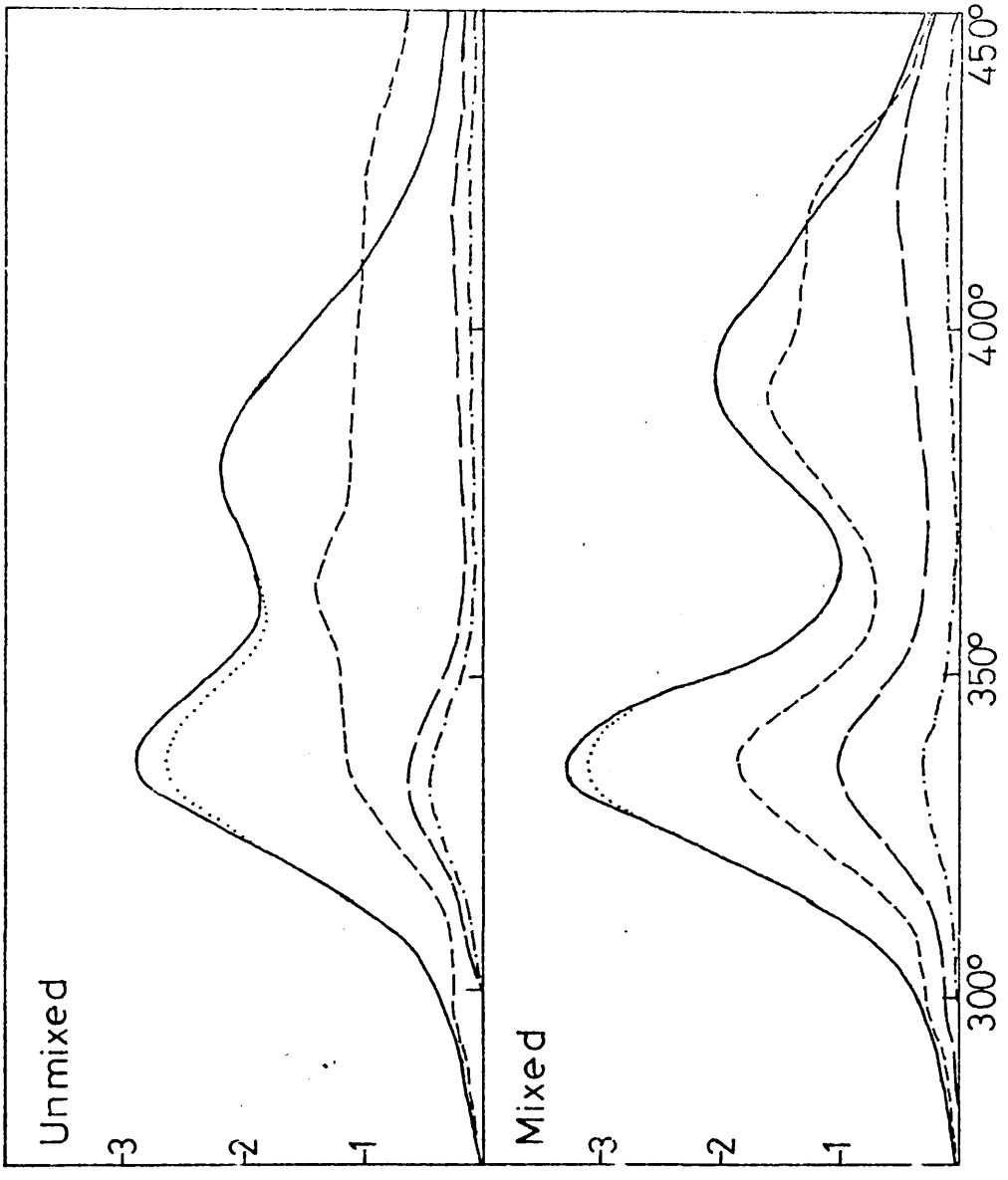


FIGURE (3.7). TVA curves for equal amounts of PMMA (An2) and PVA (BDH), (20 mg of each polymer) degraded as unmixed and mixed films at a heating rate of 10°C/Min.

(1) There is an increase in volatilization early in the degradation.

(2) In the later stages of breakdown, a smaller amount of volatile material is evolved and the T max is displaced to higher temperatures.

(3) There is a slight delay in acetic acid production.

(4) There is an increase in non-condensable production at higher temperatures.

(5) Even small amounts of PVA in the blend are capable of inducing these interactions.

(6) The interactions are characteristic of all the samples of PVA and PMMA examined, are independent of the heating rate of the experiment and of the solvent system used to prepare the films.

The interactions discussed above while quantitatively much less pronounced in PVA - PMMA blends than those observed in PVC - PMMA blends (20), are qualitatively similar, and can be interpreted in a similar fashion. Thus, the accelerated breakdown of PMMA can be explained in terms of the interaction of a radical species from degrading PVA with the PMMA macromolecule, causing chain scission of the methacrylate molecule which then undergoes depolymerization. The delay in hydrogen chloride production in PVC-PMMA was interpreted as another result of the interaction of chlorine radicals with the PMMA molecules (21). If the chlorine atoms are chain carriers in a chain reaction for PVC breakdown, then the removal in this way of even a small number of these radicals may have a significant effect on the rate of dehydrochlorination. An analogous process could be responsible for the delay of deacetylation in PVA-PMMA blends.

Also, the subsequent behaviour of PMMA at higher temperatures results from a reaction between acetic acid and the methacrylate ester groups, yielding anhydride rings within the methacrylate chains. These

anhydride units stabilise PMMA by acting as blocking groups through which the depolymerization cannot pass, and only a few such units are necessary to cause significant enhancement of stability because of the chain nature of the depolymerization reaction. The subsequent decomposition of these anhydrides and blocked methacrylate units too at higher temperatures, gives rise to the non-condensable products observed in the TVA traces above 400°C.

DEGRADATION BY THERMOGRAVIMETRY.

TG curves were obtained for PMMA and PVA as shown in figure(3.8). As can be seen, the PMMA sample which had been prepared by an anionic method, decomposes in a single stage, leaving approximately zero residual weight at 500°C. PVA, as already observed by TVA, degrades in two stages; the first stage of weight loss is due to deacetylation and accounts for approximately 70% of the sample weight: the second stage corresponds to breakdown and cyclisation of the polyenes of the carbonaceous residue, and involves a 20% weight loss.

From these curves, the curve expected for a 1 : 1 mixture by weight of PVA and PMMA was constructed by "addition". This is compared, with the actual experimental TG curve for the mixture, in figure (3.9). The weight loss behaviour from the blend is different from that expected in the absence of any interactions. In the initial stages of reaction, the curves are almost identical, while between 350°C and 400°C, the mixture shows increased stability. Above 400°C, approximately, the curves close together again.

Thus, while the stabilisation at higher temperatures of the mixed samples is confirmed by TG, there is only little evidence to suggest the increased volatilization, observed by TVA, early in the degradation. This is not unreasonable when it is considered that the polymers in the mixed samples in these experiments were in the form of powders, since the Du Pont instrument is not suitable for th-

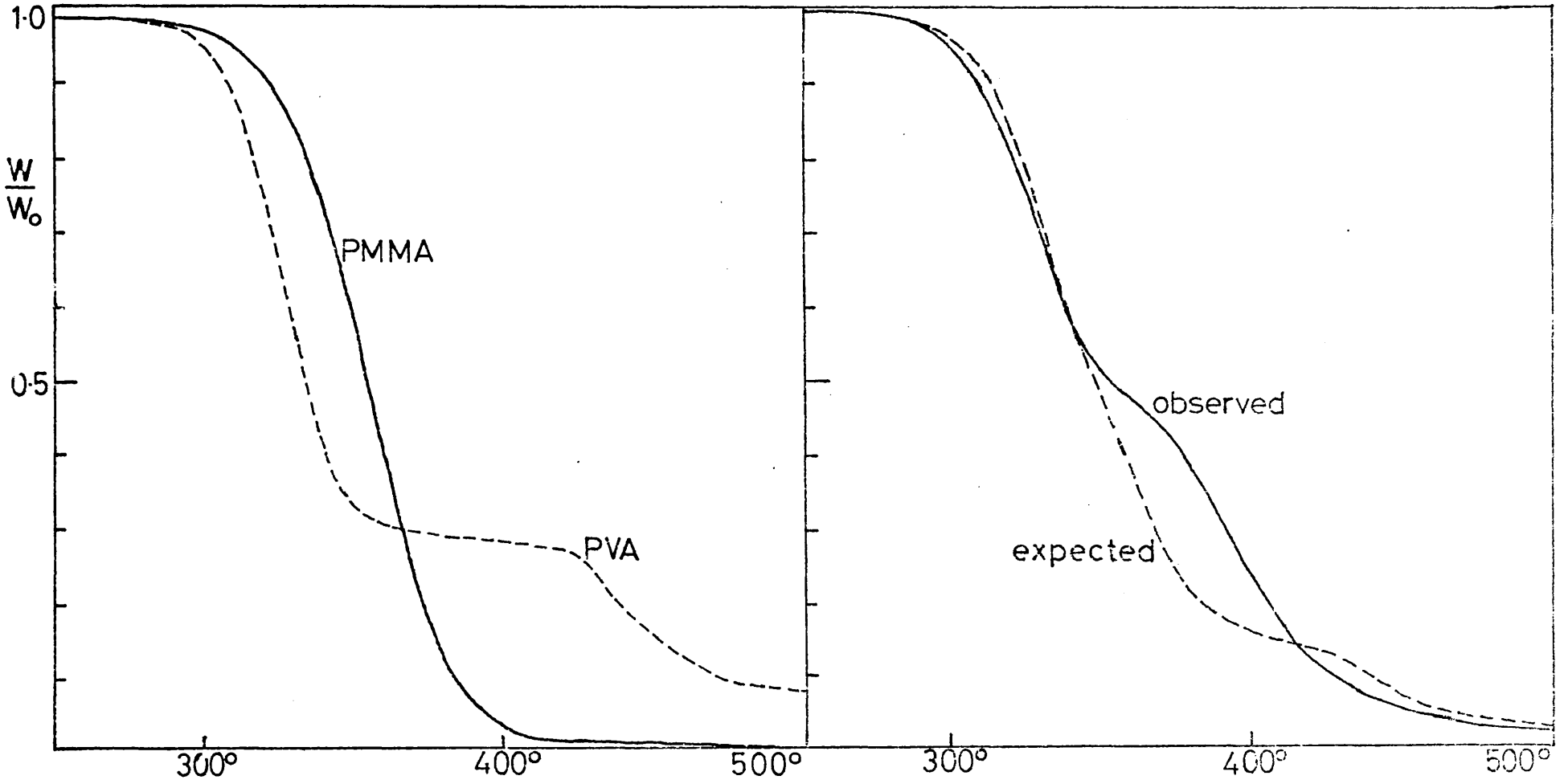


Figure (3.8). TG curves for PMMA(An 2) and PVA (BDH) under dynamic N_2 flow. Samples as 10 mg Powders. Heating rate 5°C/min.

Figure (3.9). Comparison of "expected" and experimentally observed TG curves for a 1:1 mixture of PMMA(An 2) and PVA (BDH). Heating rate 5°C/min.

study of film samples. Hence, while it is still possible that acetic acid from degrading PVA can react with the methacrylate ester groups by diffusing through molten polymer, the contact between the two unlike polymer species may not be intimate enough to allow reactive radicals from degrading PVA to interact with the PMMA. Similar results have been obtained by McNeill and Neil (20) for TG studies of PVC - PMMA mixtures.

INFRA-RED ANALYSIS OF VOLATILE PRODUCTS.

I.R. spectra were obtained of the gaseous degradation products from mixed film samples of PVA and PMMA of various ratios. The sample sizes were 100 mg, and degradations were carried out at $10^{o}C$/min. to $500^{o}C$ under normal TVA conditions, except for analysis of products non-condensable at $-196^{o}C$, when a closed system was used. In order that residual solvent from the films would not be included, the cold traps were raised only when all the solvent had escaped from the film. Since acetic acid and methyl methacrylate were the major products and tended to obscure other minor products, a fractionation procedure was employed to condense these products at $-80^{o}C$. Thus spectra were obtained of products condensable at $-80^{o}C$, products non-condensable at $-80^{o}C$ but condensable in liquid nitrogen at $-196^{o}C$, and using the closed system, products non-condensable at $-196^{o}C$.

The results of these analysis are shown in Table (3.2) and the spectrum of a fraction non-condensable at $-80^{o}C$ is shown in figure (3.10). Carbon dioxide can be recognised from its typical absorptions, above 3600 cm^{-1}, at 2320-2345 cm^{-1} and below 700 cm^{-1}; ketene may be identified by its triplet peaks at 2138, 2150 and 2162 cm^{-1}, while methanol has its typically sharp peak at 1031 cm^{-1}. The absorptions of methyl acetate and methyl methacrylate overlap in

TABLE (3.2)

Volatile products from degradation of PVA-PMMA blends, observed by I.R.

Condensable at -80°C	Non condensable at -80°C	Non-condensable at -196°C
Methyl methacrylate Acetic Acid Methanol) Methyl Acetate) Trace	Carbon dioxide Ketene Methyl acetate Methanol Methyl Methacrylate Unsatd.Hydrocarbons(?)	Methane Carbon monoxide Ethylene (?)

in many places, but the absorptions at 1778 and 1760 cm^{-1} (C=O stretching vibrations) and at 1245 cm^{-1} (C-O stretching vibration) can be attributed to methyl acetate, while those absorptions at 3090 cm^{-1} (C-H stretching), 1750 and 1740 cm^{-1} (C=O stretching) and 1166 cm^{-1} (C-O stretching) are those of methyl methacrylate. This was confirmed by examining separately, standard gaseous samples of methyl acetate and methyl methacrylate by expansion of each into an evacuated I.R. gas cell. The absorptions and relative intensities are given in Appendix One. In figure (3.10), the only region of absorption which cannot definitely be accounted for, is around 900 cm^{-1}, although this probably results from the presence of some unsaturated hydrocarbons including ethylene.

The cold ring fraction from degradation of mixed samples was also examined and was found to be identical to that obtained from the degradation of PVA. This consists of low molecular weight polymor, presumably arising from scission reactions, which contains evidence of unsaturation from deacetylation. Thus apart from methyl acetate and methanol, the other products listed in Table (3.2) are obtained from degradation of the homopolymers themselves.

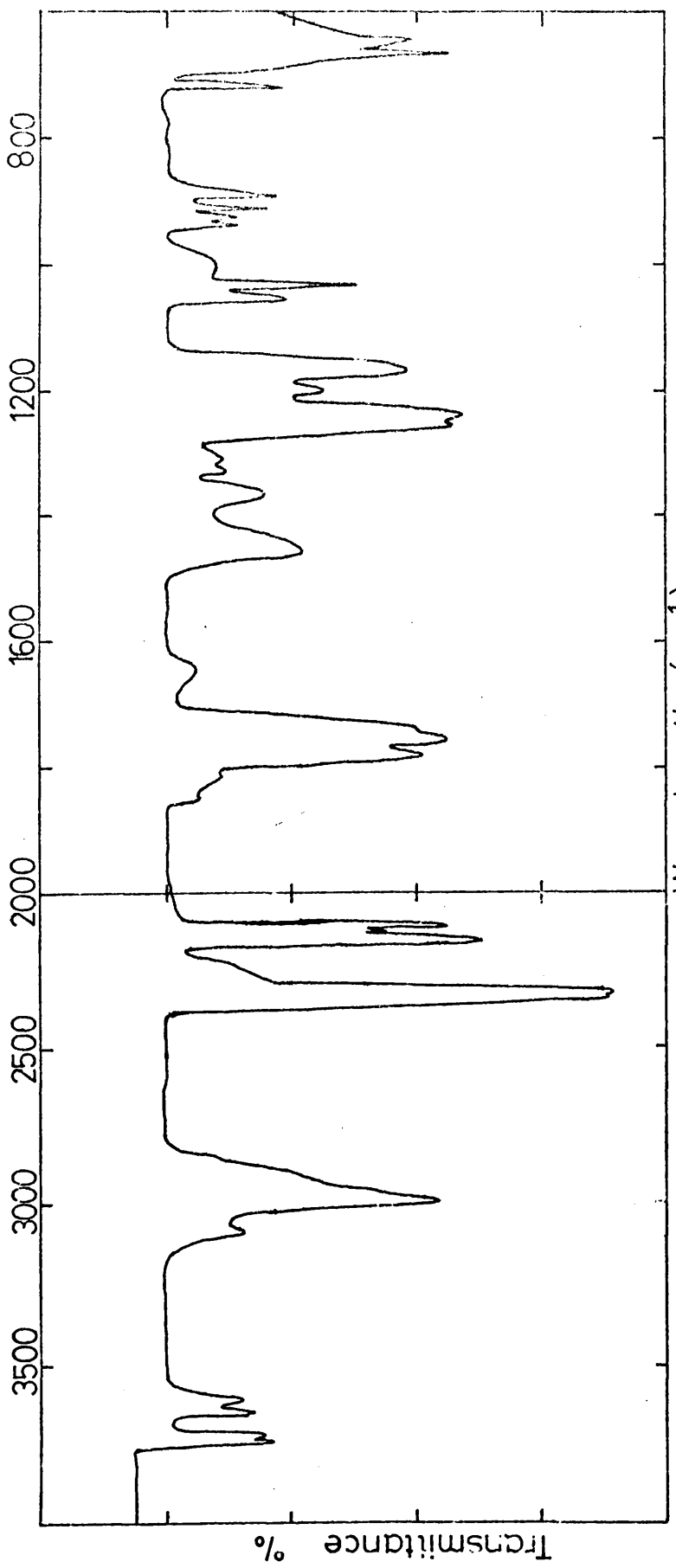


Figure (3.10). Infra-red spectrum of the products of degradation (non-condensable at -80°C) of a PMMA (An 2) - PVA (BDH) mixed film, degraded at 10°C/min to 500°C.

MASS SPECTROMETRIC ANALYSIS OF VOLATILE PRODUCTS

Analysis, by mass spectroscopy of volatile products condensable at -196°C was carried out using similar degradation techniques as for the infra-red analysis. Products were fractionated at -80°C, collected by distillation into a suitable gas sampling bulb and the mass spectra obtained for the samples as gases, on an AEI MS12 mass spectrometer operating at 20 eV. The spectra for the two fractions are shown in figure (3.11) and interpretation of these spectra is presented in Table (3.3).

For the products condensable at -80°C, methyl methacrylate and acetic acid are present: there are also traces of methyl acetate and methanol and other products (benzene, cyclohexene and various unsaturated hydrocarbons) which probably arise from breakdown of the aromatic and cyclic structures in the carbonaceous residue of PVA deacetylation. It should be noted that several peaks of particular M/E valve can be assigned to more than one product, e.g. 59 - $\cdot CO_2CH_3$: this fragment can arise from methyl methacrylate or methyl acetate and similarly, 43 - CH_3CO, can result from acetic acid or methyl acetate. The products non-condensable at -80°C, but condensable at -196°C, contain methyl methacrylate, methanol, methyl acetate, ketene and carbon dioxide in substantial amounts, as well as products from breakdown of the carbonaceous PVA residue. On the whole, the evidence of mass spectrometric analysis is in agreement with that obtained by infra-red.

TABLE (3.3)

Assignment of Peaks from mass spectra of Volatile products.

Products condensable at -80°C		Products non-condensable at -80°C	
M/E	PRODUCT	M/E	PRODUCT
100,69,59,41,15	Methyl methacrylate	100,69,41	Methyl methacrylate
43,42,29,15	Acetic Acid	74,59,43,42,29	Methyl Acetate
74,59,43,42,29	Methyl acetate	31,32,20,28	Methanol
31,32,29,28,18	Methanol	44,28	Carbon Dioxide
44,28	Carbon Dioxide	42,41	Ketene
56,55,54	Butene	56,55,54	Butene
82	Cyclohexene(?)	78	Benzene
78	Benzene		

ANALYSIS OF PRODUCTS BY GAS-LIQUID CHROMATOGRAPHY

GLC analysis was performed on liquid volatiles, (without product fractionation), from TVA degradation at 10°C/min to 500°C of a mixed 100 mg film containing equal amounts of each polymer. The instrument employed was the Microtek GC 2000 R Research Gas Chromatograph equipped with a flame ionization detector with nitrogen as carrier gas. A 1% Carbowax column was used isothermally for an initial period and then with temperature programming at 10°C/min.

A typical chromatogram is reproduced in figure (3.12). Peaks A and B had the same retention time as methyl acetate and methanol respectively, while peak C was identified as methyl methacrylate. The final peak D which was strongly retained on the column was identified as acetic acid. The shoulder on the leading edge of the methyl methacrylate peak (C) was not definitely identified, but had a similar retention time to benzene which was identified in the mass spectra, and which arises from breakdown of the PVA carbonaceous residue.

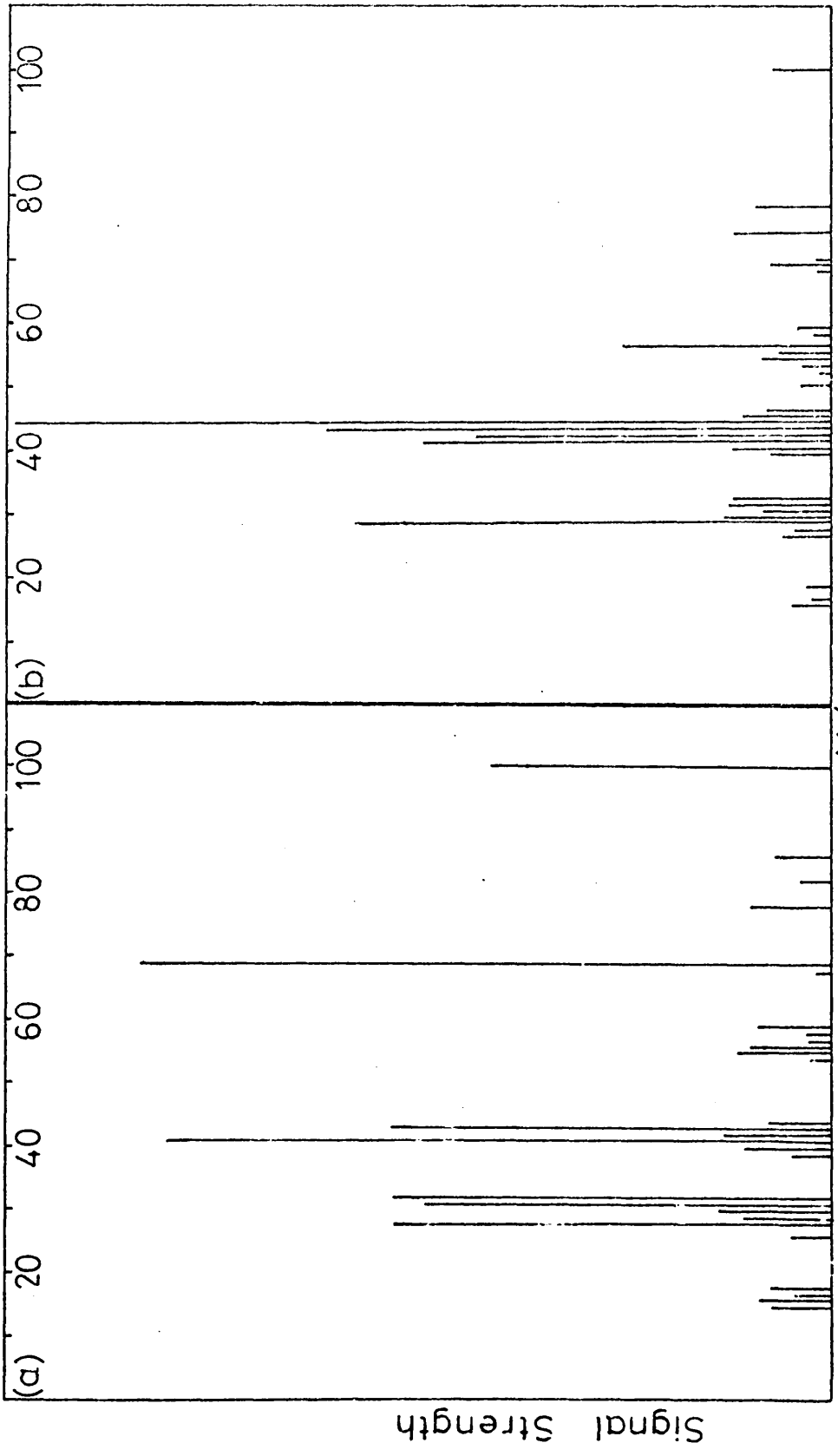


Figure (3.11). Mass spectra of the products of degradation of a 5:1 PMMA (An2) - PVA (BDH) mixed film, degraded at 10°C/min to 500°C.
(a) products condensable at -80°C. (b) products non-condensable at -80°C.

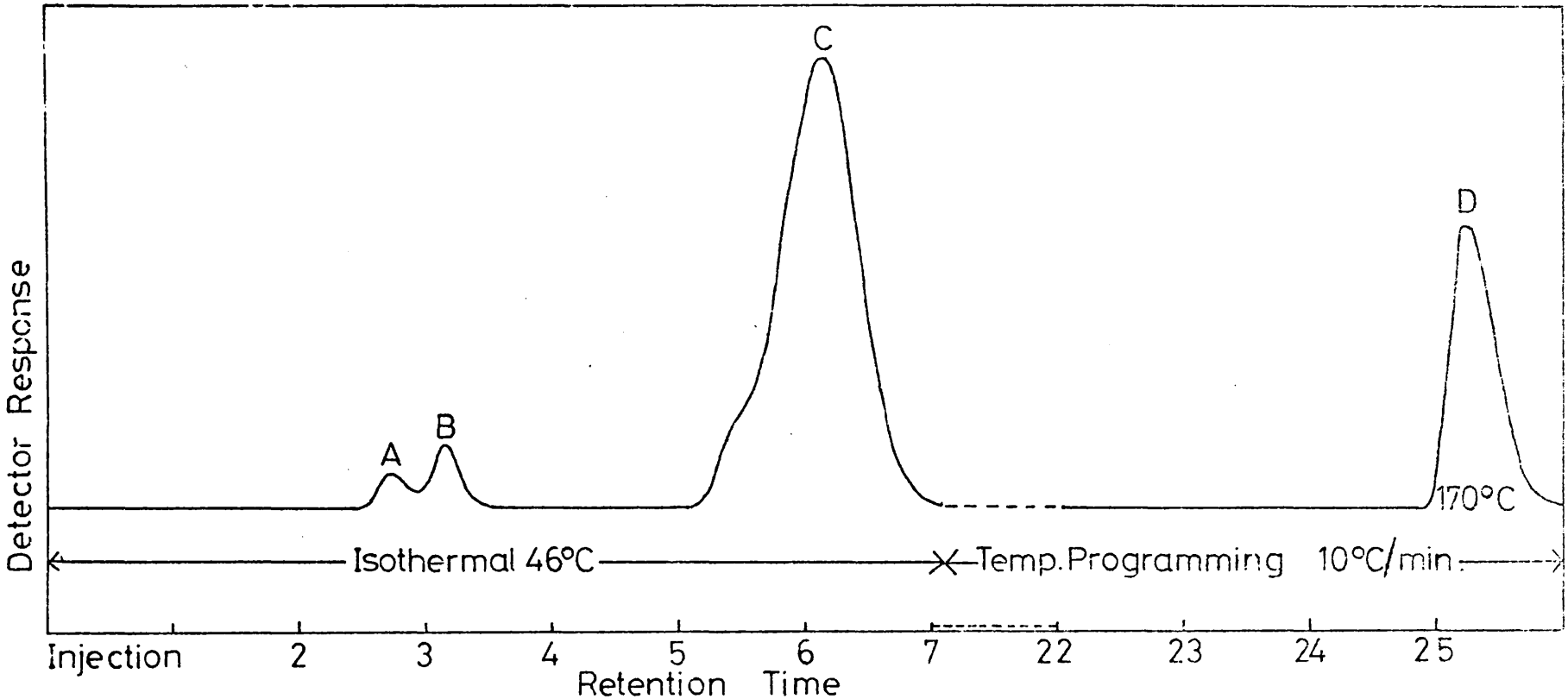
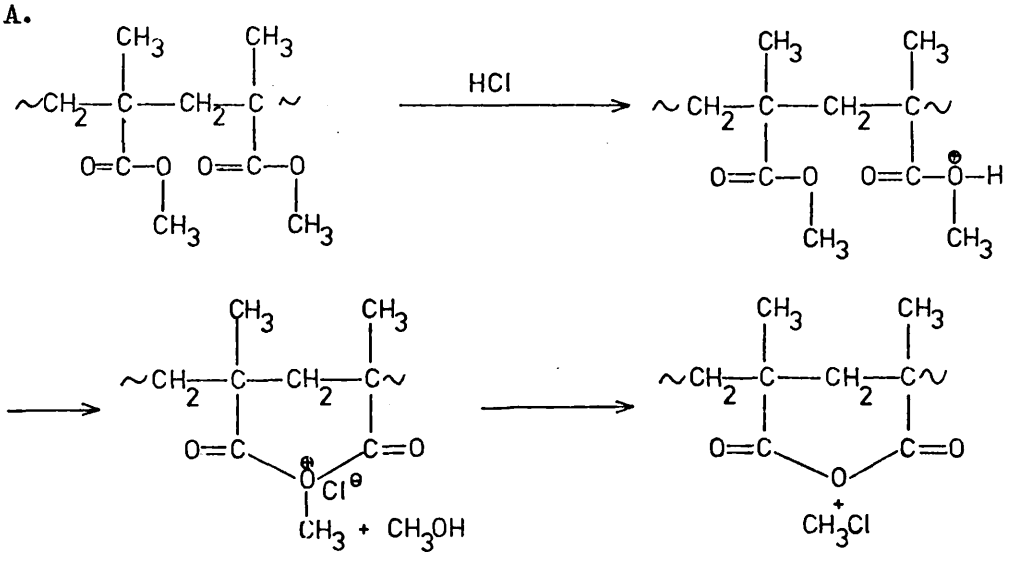


Figure (3.12). GLC Chromatogram of the liquid degradation products of a mixed film of equal amounts of PMMA (An2) and PVA (BDH).
Heating rate of degradation 10°C/min, to 500°C.

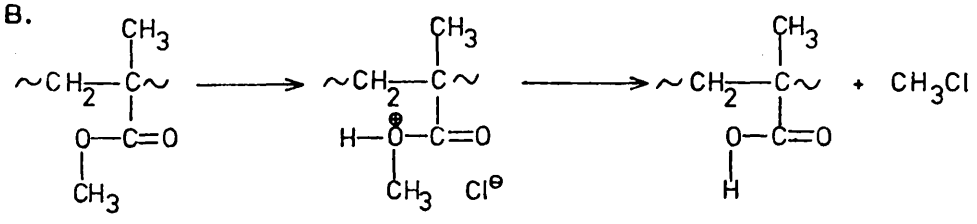
SUMMARY OF VOLATILES ANALYSIS

Apart from methyl acetate and methanol which are present only in very small amounts, the products obtained from degradation of PVA-PMMA mixtures are those expected from the decomposition of the respective homopolymers. The origin of these two substances can be found by analogy with the production of methyl chloride and methanol by the action of hydrogen chloride on the ester group of PMMA in polychloroprene - PMMA blends (27). McNeill and Neil (21) postulated two possible mechanisms for the action of hydrogen chloride on PMMA. The first of these requires the formation of both methyl chloride and methanol, while the second only requires the formation of methyl chloride (and water) and was suggested as an alternative, since McNeill and Neil failed to detect methanol among the volatile products from PVC - PMMA blends (21). In the second case formation of anhydride structures was thought to occur by dehydration of pairs of adjacent methacrylic acid groups.

A.



B.



Since they detected both methyl chloride and methanol in the degradation of polychloroprene - PMMA blends, Gardner and McNeill (27) concluded that mechanism A was valid. Thus it is possible that the formation of methyl acetate and methanol in PVA - PMMA blends, is due to the interaction of acetic acid with the PMMA ester groups. However the mechanism of anhydride formation will be discussed in more detail, later in this chapter.

QUANTITATIVE ESTIMATION OF ACETIC ACID.

The delay in production of acetic acid from PVA - PMMA blends was shown by estimation of acetic acid produced by degradation of (a) PVA alone and (b) PVA - PMMA blends. The technique involved degrading PVA homopolymer as a film to a certain extent and then degrading a mixed film of PVA (BDH) and PMMA (R1) to the same extent of degradation. In each case, the acetic acid produced was collected and litrated with $^{N}/_{100}$ sodium hydroxide using phenolphthalein as indicator.

Figure (3.13) illustrates results from two different series on experiments. In figure (a) the amounts of acid produced (in terms of NaOH required for neutralization) at various temperatures during temperature programmed degradation experiments at $5^{o}C$/min are shown. As may be seen, there is a slight delay in the production of acid from the blend compared with that from the homopolymer on its own, although the total amount of acid produced is the same in either system.

Isothermal experiments were carried out at $275^{o}C$ and figure (3.13) (b) shows the rate of production of acetic acid at various times from both systems. The values of the deacetylation rates are the result of thirty-two separate acetic acid estimations and again, the slight delay in production of acetic acid from PVA blended with PMMA is observed.

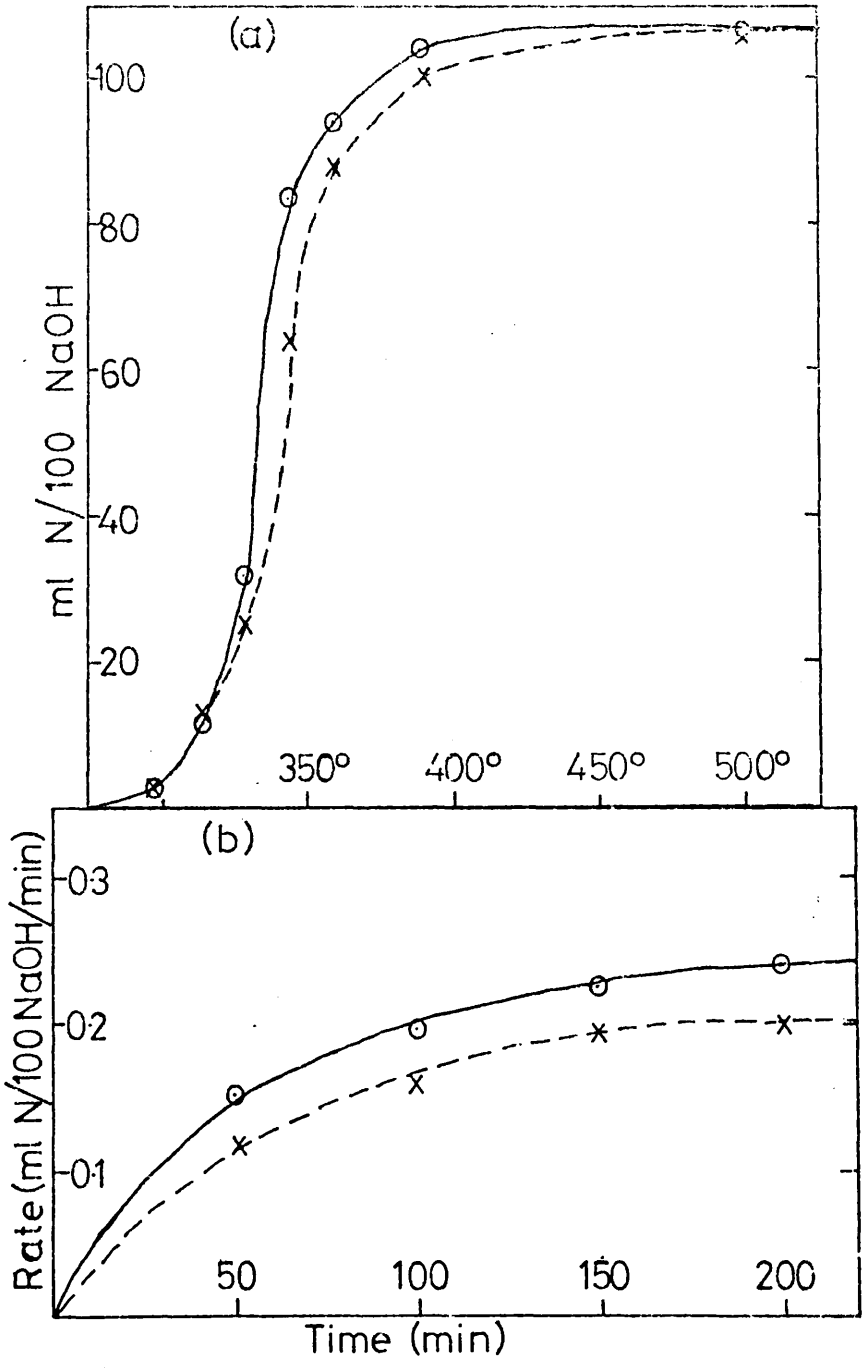


Figure (3.13). Estimation of acetic acid produced from degradation of PVA (BDH) and from PVA(BDH)-PMMA(R1) Blends.

(a) temperature programming at 5°C/min.

(b) isothermal at 275°C.

—o—o— Acetic acid from PVA

– x – x – Acetic acid from PVA-PMMA Blends.

These observations are thus in agreement with the TVA evidence and are analogous to the situation in PVC-PMMA blends where delay in hydrogen chloride production is apparent.

STRUCTURAL CHANGES OCCURRING IN PMMA DURING DEGRADATION OF THE BLENDS.

MOLECULAR WEIGHT CHANGES.

A comparison was made of molecular weight changes during degradation of PMMA (R2) and of PMMA (R2) extracted from a 5:1 PMMA-PVA(BDH) mixture degraded to the same extent. A sample of 150 mg of PMMA in the form of a film was heated at 270°C for 60 minutes under vacuum and then rapidly cooled. The residue was dissolved in A.R. grade toluene, and the concentration of the solution estimated by evaporating to dryness a known weight of solution and determining the weight of polymer present. The molecular weight was determined by osmometry.

The same weight of PMMA was then heated under similar conditions as a mixed film with 30 mg of PVA. The residue, which was brown in colour was removed from the degradation tube and extracted with toluene with continuous stirring, over a period of 24 hours. At no stage were the toluene extracts heated, and since PVA rapidly becomes insoluble even after small extents of degradation (10), it was assumed that the polymer removed from the degraded blend by toluene extraction consisted almost exclusively of PMMA. This was confirmed by degrading PVA samples under similar conditions and extracting the residue with toluene. It was found that at these extents of degradation (11% weight loss, 16% deacetylation), PVA was completely insoluble in toluene and thus the assumption made was valid. The results of this investigation are shown in Table (3.4) and it is clear that in the presence of thermally degrading PVA, (as in the case of PVC (21)), PMMA samples undergo a more rapid fall in

molecular weight compared with that for PMMA degraded on its own.

TABLE (3.4)

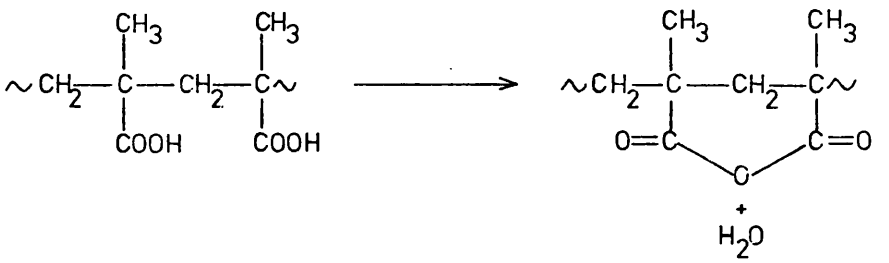
The effect on the molecular weight ($\overline{Mn}$) of PMMA (R2) for samples heated at 270°C for 60 minutes, alone and as a mixed film with PVA (BDH). (PMMA original $\overline{Mn}$, 675,000).

Expt.	$\overline{Mn}$ after heating alone	$\overline{Mn}$ after heating with PVA
1.	326,000	80,000
2.	310,000	82,000
3.	345,000	86,000

INFRA-RED ANALYSIS

Spectra of PMMA (R1) degraded at 5°C/min to 350°C were obtained by dissolving the residue in toluene and casting a film from the solution on to a sodium chloride disc. Mixed films of PMMA (R1) containing an equal amount of PVA (BDH) were degraded under similar conditions and spectra of the PMMA residue obtained using a similar extraction procedure as before. In figure (3.14), the regions of the spectrum in which changes occur between the two PMMA samples, are compared.

The bands which develop in the sample degraded as a blend with PVA, at 1800 cm^{-1} (and a shoulder at 1762 cm^{-1}) and at 1018 cm^{-1} , are frequencies similar to those found in anhydro-poly (methacrylic acid) which is formed from pyrolysis of poly(methacrylic acid), (15),



Grant and Grassie (15) related the presence of the twin carbonyl peaks at 1795 cm^{-1} and 1750 cm^{-1} , and the C-O-C stretching

vibration at 1022 cm^{-1} , in the spectrum of degraded poly (methacrylic acid), to the six-membered ring anhydride structure shown above. McNeill and Neil found similar absorptions for PMMA extracted from partially degraded PVC-PMMA blends (21). These spectra thus provide a strong indication that anhydride rings may be present in PMMA which has been degraded in the presence of PVA.

The other major difference between the spectra in figure (3.14) is the presence of a broad band at 3600-270 cm^{-1} in the sample of PMMA extracted from the mixed system. Pure poly(methacrylic acid) has a broad peak in this region due to the presence of "bonded" hydroxyl groups. Therefore, besides the anhydride rings, there is a strong possibility that free methacrylic acid groups also occur in PMMA degraded with PVA.

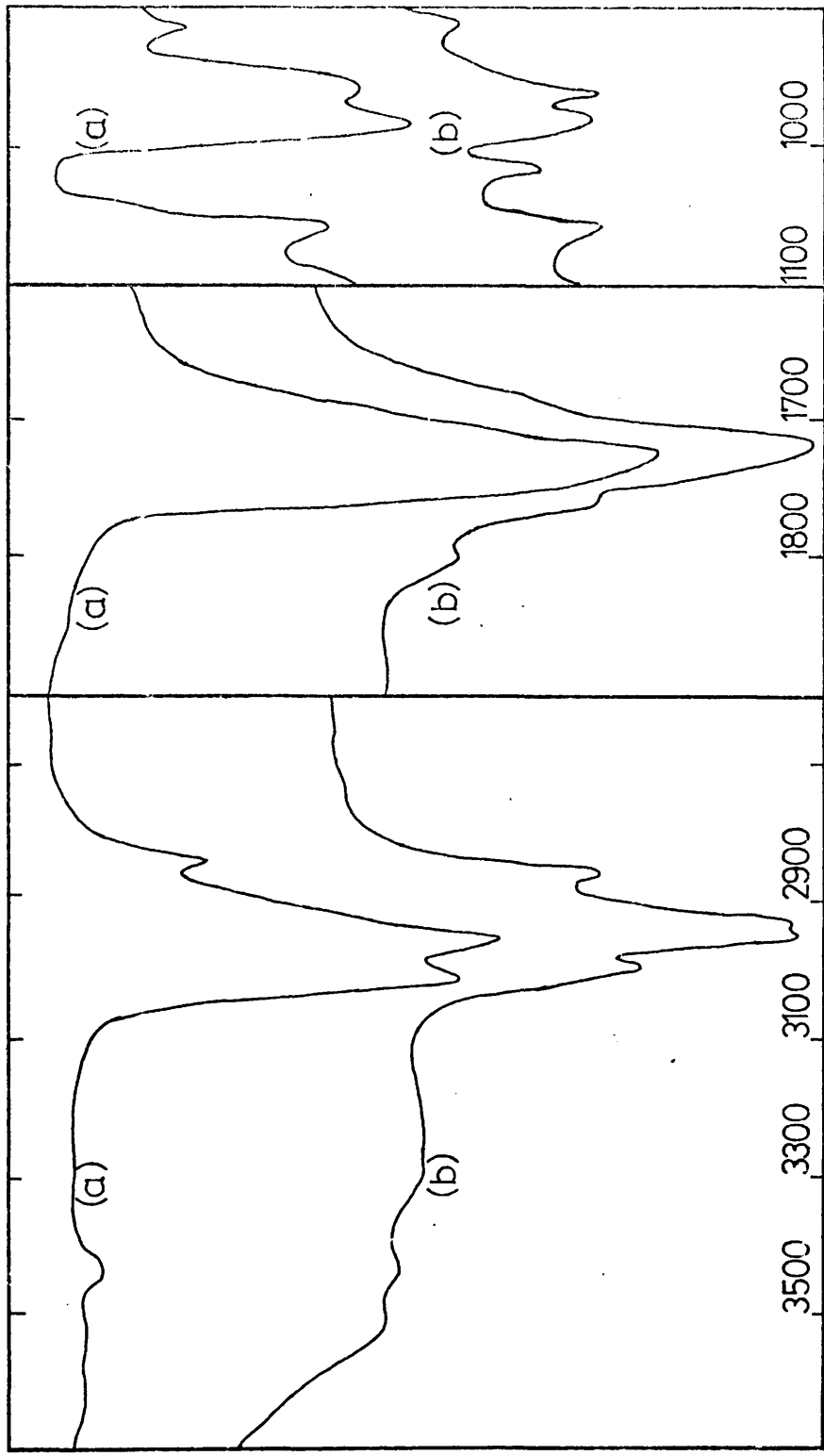


Figure (3.14). IR spectra of PMMA (R1) residues extracted from degradation at 5°C/min. to 330°C,

(a) from PMMA heated alone
(b) from PMMA heated with an equal amount of PVA (BDH).

TVA INVESTIGATION OF DEGRADED PMMA SAMPLES

TVA traces of PMMA samples, partially degraded under varying conditions were compared with TVA traces of PMMA samples partially degraded under similar conditions but in the presence of PVA. In figure (3.15) TVA traces of PMMA (An2) samples degraded to 350°C at 5°/min. alone and with an equal amount of PVA (BDH) are compared. The differences in behaviour of the two samples are similar to those found by McNeill and Neil (21) for PVC-PMMA blends; viz. the PMMA peak is displaced to higher temperatures in the sample extracted from the blend (370°C to 390°C) and there is also an increase in the production of products non-condensable at -100°C around 400°C in the sample extracted from the blend: this sample also left a black residue after degradation in the TVA apparatus. These effects have been reported previously as being characteristic of the TVA degradation of poly(methacrylic acid) (34).

Similar TVA studies were made on PMMA (R1), except that the partial degradations were carried out isothermally at 250°C for 100 min, and these TVA traces are shown in figure (3.16). The double peak of the sample extracted from the mixed system is comparable to TVAs for PMMA samples of low molecular weight prepared by a free-radical process (7), the first peak arising from monomer production by initiation at unsaturated chain ends. This situation was also observed and accounted for by McNeill and Neil (21) who proposed a mechanism for increased monomer production from PMMA in PVC-PMMA blends which suggests chain scission of the methacrylate macromolecules accompanied by formation of double bonds at "new" chain ends. The effects observed in figure (3.16) are thus consistant with the molecular weight behaviour noted previously and are in other respects similar to those effects noted in figure (3.15), apart from the appearance of material non-condensable at -100°C at lower temperatures. In fact these non-

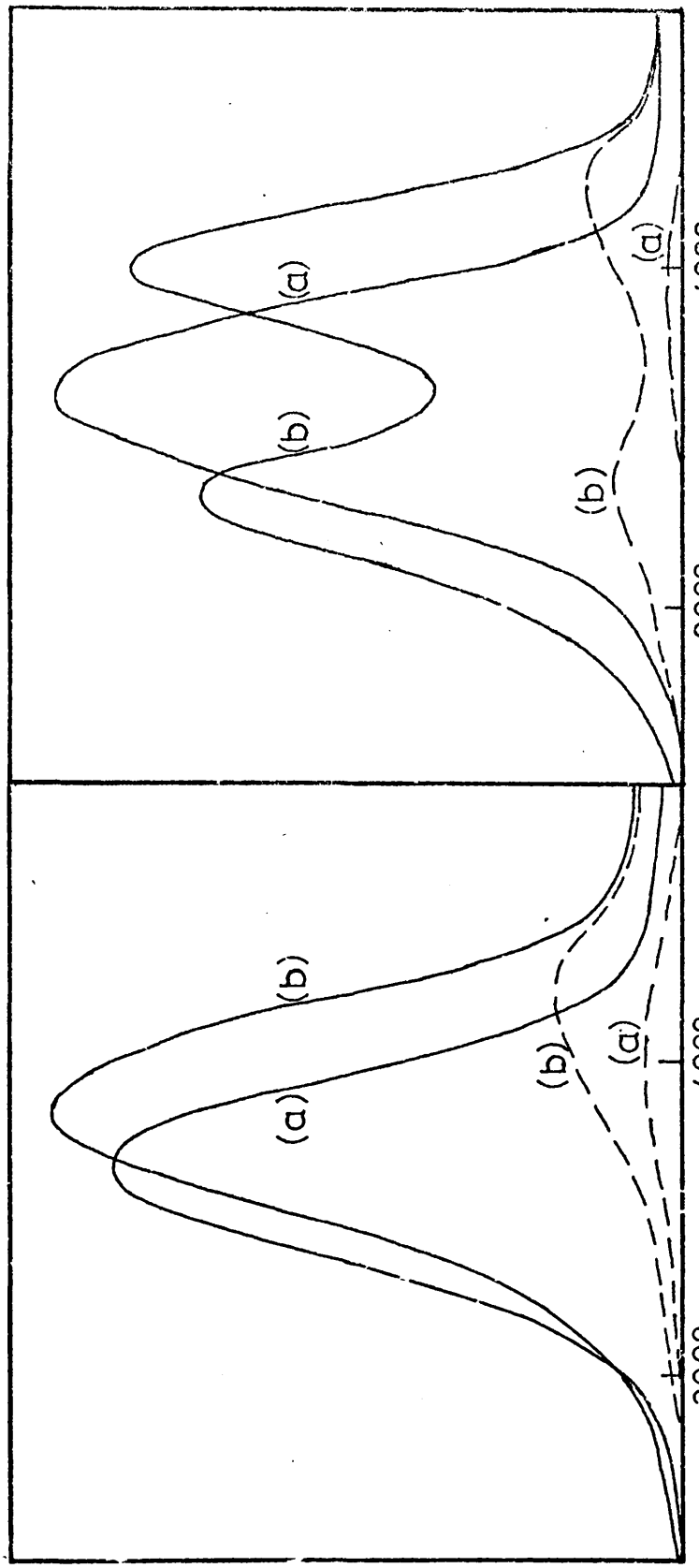


Figure (3.15). TVAs (10°C/min) of PMMA (An2) samples (a) previously degraded to 350°C at 5°C/min, (b) previously degraded at 350°C at 5°C/min with PVA (BDH). Only 0°C and -100°C traces shown.

Figure (3.16) TVAs (10°C/min) of PMMA (R1) samples (a) Previously degraded at 250°C for 100 min, (b) previously degraded at 250°C for 100 min with PVA. Only 0°C and -100°C traces shown.

condensable products are produced at temperatures as low as 300°C and may be due to the production of methyl acetate and methanol which both exhibit limiting rate behaviour at -100°C.

SUMMARY OF STRUCTURAL CHANGES IN PMMA.

Information on the structural changes induced by PMMA by heating as a blend with PVA may be summarized as follows :-

(a) The I.R. spectrum shows acid and anhydride structures in the residue.

(b) The molecular weight falls more rapidly than in PMMA degraded on its own.

(c) The polymer leaves a black residue after degradation by TVA.

(d) TVA shows a shift of the main degradation peak to higher temperatures.

(e) Some products, non-condensable at -100°C and -196°C are obtained around 400°C in the TVA trace.

(f) Polymer from isothermal degradation at 250°C shows an additional peak at 320°C in the TVA and there is simultaneous production of material non-condensable at -100°C.

EFFECT OF ACETIC ACID ON PMMA

McNeill and Neil (21), (and Gardner and McNeill(27)), found, by IR analysis and by TVA, that heating PMMA in the presence of gaseous HCl, produced anhydride ring structures in the PMMA chain and resulted in the same features of degradation as PMMA extracted from a blend with PVC. This led to postulated mechanisms of interaction of HCl with PMMA shown earlier.

The effect of gaseous acetic acid from PVA deacetylation, on PMMA heated in its presence, was negligible, probably because the acetic acid tended to condense on the cooler parts of the degradation

apparatus. PMMA was then heated for 150 minutes in refluxing toluene solution containing glacial acetic acid which had been dried over magnesium sulphate for two days. The amount of acetic acid employed was that which would be produced from a weight of PVA, equal to the amount of PMMA used. The refluxing temperature was approximately 112°C and the experiments (duplicated) were repeated without the acetic acid. For each experiment, the PMMA was precipitated into petroleum ether, filtered, washed with more precipitant and dried under vacuum for 24 hours. The polymer samples were then analysed by TVA, IR spectroscopy and by determination of molecular weight.

The TVA curves, IR spectra and molecular weights of the PMMA treated without acetic acid were all identical to those for the original sample. The TVA traces for the samples treated in the presence of acetic acid were only slightly different from those for the original sample in that a small peak appeared around 400°C for products non-condensable at -100° and -196°C. The IR spectra of these samples exhibited absorptions in the region of 3600-3100 cm^{-1}, indicating the presence of acid groups, although there was no absorption typical of anhydride units. The molecular weights were identical to the original sample.

The small effects observed and the low temperatures at which these experiments were carried out, mean that it is impossible to offer more than tentative interpretations of the effect of acetic acid on PMMA in this system compared with that in the degradation of the polymer mixtures. However, from the IR evidence it appears that this treatment of PMMA with acetic acid in refluxing toluene produces acid groups within the polymer chain and that these acid groups are converted, during TVA degradation, to anhydride rings which produce the non-condensable peaks in the TVA traces. Also it

is possible that traces of water remained in the acetic acid even after the drying procedure, and that the water was involved in an acid hydrolysis of the ester groups, but it should be remembered that during the deacetylation of PVA, small quantities of water are produced. Thus if acid groups are formed in these experiments as well as in PMMA degraded as a blend with PVA (as the IR evidence suggests), then it may be acetic acid and water, or merely acetic acid itself which is responsible for the hydrolysis reaction. It must be admitted, however, that the evidence for these interpretations is not conclusive.

DISCUSSION

As considered by McNeill and Neil for PVC-PMMA blends (21), it is not possible to account for the interaction processes and changes in PMMA structure in terms of a single type of interaction. However, it will be shown that the simultaneous occurrence of two interactions could provide an adequate explanation.

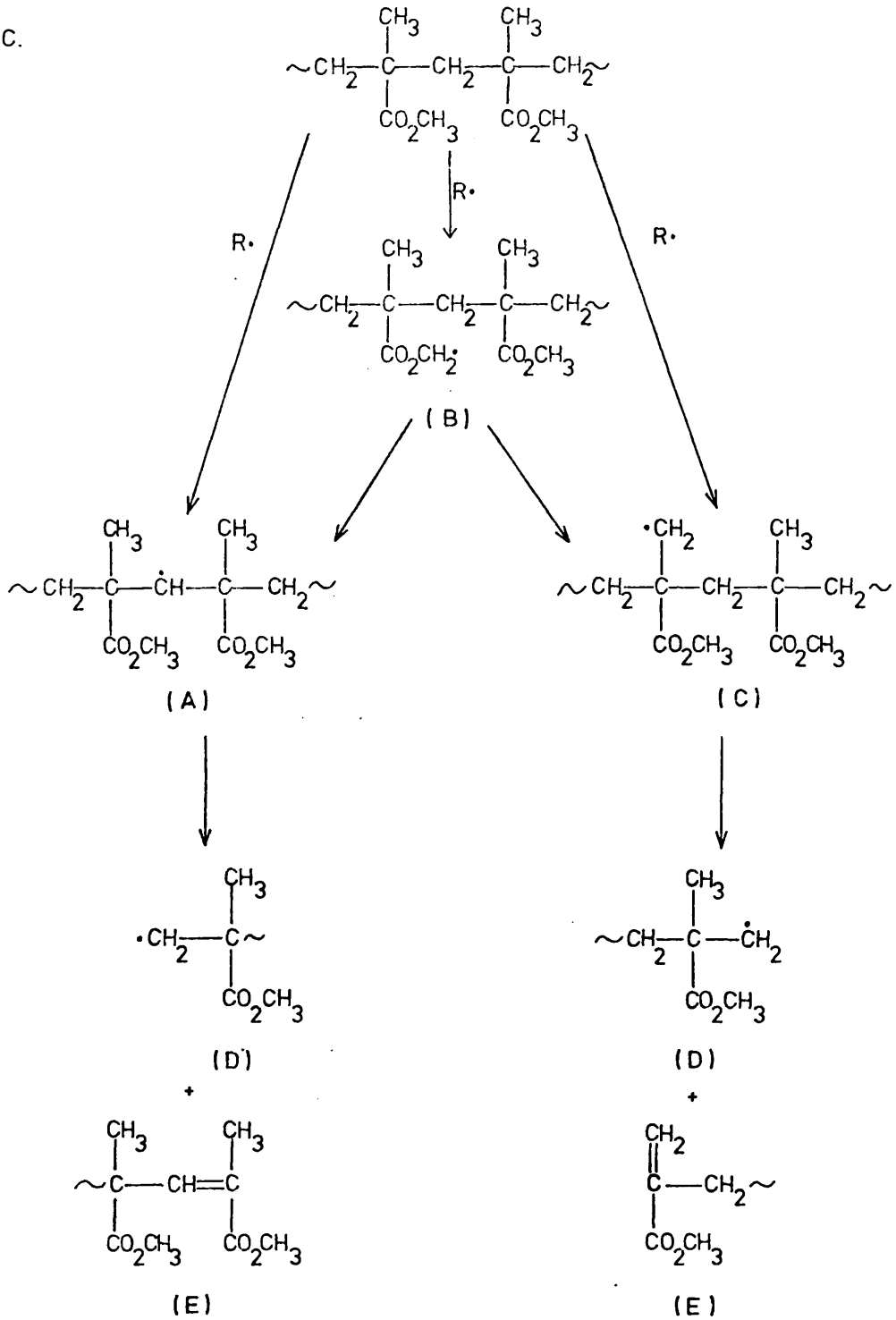
INCREASED MONOMER PRODUCTION FROM PMMA AND CHAIN SCISSION

In chapter one a reaction sequence was outlined for these processes which took place in PVC-PMMA blends. This involved chlorine radical attack on PMMA, via a hydrogen abstraction process, leading to subsequent chain scission and depropagation. From the evidence collected, it would appear that a similar process is taking place in PVA-PMMA blends, where the chain scission reaction can account for the molecular weight fall, while the subsequent depropagation leads to monomer production.

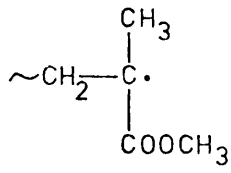
Since films of PVA-PMMA mixtures were opaque and heterogeneous indicating an incompatible system, any species formed during the decomposition of PVA must, in order to react with a PMMA molecule, be capable of migrating across a phase boundary. Since the motion of the PVA polymer radical is severely restricted (and this is also

aggravated by the rapid cross-linking of PVA), it is much more likely that the attacking species will be a small radical, or a small molecule which can diffuse from one domain to the other; and then undergo some form of radical reaction. McNeill and Neil's reaction scheme (21) for the attack of a small radical species on PMMA is shown in mechanism (C).

C.



McNeill and Neil concluded that radical (D) was capable of depolymerizing to monomer. Although the depolymerizing radical is usually thought to have the same structure as the polymerizing radical (F), there is no evidence to suggest that radicals of type (D) cannot depropagate, although it may be more likely to give transfer (5).

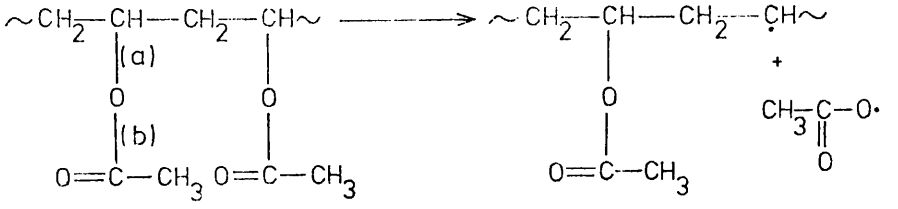


(F)

This mechanism can therefore account for production of monomer and chain scission, but it also predicts that unsaturated molecular chain ends are produced during the reaction. These structures have been revealed by TVA examination of PMMA extracted from a PVA-PMMA mixed film which had been partially degraded isothermally at 250°C, (figure (3.1b)).

The outstanding problem on this reaction scheme is the identity and origin of the small radical species R•. While in the PVC-PMMA system, the interacting radical species involved is easily recognised, in the case of PVA-PMMA mixtures, both the nature and origin of the interacting radical are not immediately obvious. Also, in this system, account must be taken of both the origin and mechanism of formation of the other volatile products detected besides acetic acid, viz. ketene, water, CO_2, CO and CH_4, and it is possible that these two phenomena are inter-related. Two possible explanations of these effects may be considered.

The first involves postulating a radical mechanism for PVA deacetylation as shown below.



Grassie (1) considers bond (a) to be weaker than bond (b) and hence the formation of acetate radicals is preferred to that of acetyl radicals, CH_3CO. Migration of the acetate radical to the PMMA domain would provide the required radical interactions and the two possible reactions shown below.

$$CH_3COO\cdot + PH \longrightarrow CH_3COOH + P\cdot \qquad (1)$$

$$CH_3COO\cdot + PH \longrightarrow CH_4 + CO_2 + P\cdot \qquad (2)$$

The first reaction is a simple hydrogen abstraction to form acetic acid, while the second has been postulated by Burton (51) as a low activation energy step in the photolysis of acetic acid vapour. The formation of the minor products can arise either from the decomposition of acetic acid, which will be discussed later, or from breakdown of the radical $CH_3COO\cdot$ as shown below

$$CH_3\overset{O}{\overset{\|}{C}}-O\cdot \longrightarrow CH_2{=}C{=}O + \cdot OH \ (\xrightarrow{H} H_2O)$$

$$\longrightarrow CO_2 + CH_3 \ (\xrightarrow{H} CH_4)$$

$$\xrightarrow{?} CO$$

The second possible explanation of the nature and source of the interacting radicals involves the suggestion that acetic acid undergoes radical decomposition as it diffuses through the molten polymer mass. The thermal decomposition of acetic acid has been investigated by Bamford and Dewar (52) who pyrolysed acetic acid by a flow method in quartz tubes in the temperature range 500°- $900^{\circ}C$.

It was suggested that the significant reactions occurring were :-

$$CH_3\,CO_2\,H \longrightarrow CH_2 = C = O + H_2\,O \quad (1)$$

$$CH_3\,CO_2\,H \longrightarrow CH_4 \quad (2)$$

$$2\,CH_2 = C = O \longrightarrow CH_4 + C + 2\,CO \quad (3)$$

$$2\,CH_2 = C = O \longrightarrow C_2\,H_4 + 2\,CO \quad (4)$$

While both reactions (1) and (2) were found to be homogeneous and of the first order, it was observed that at the lower temperatures decomposition of ketene and decarboxylation were less important and that the conversion to ketene was 2% at 487°C. More recently, Scotney (53) has observed decomposition of acetic acid to ketene in silica tubes at temperatures as low as 380°C using both vacuum techniques and an argon flow system. Also, at 322°C, during the vacuum degradation of cellulose triacetate, Scotney (53), observed the production of ketene which he suggested arose from decomposition of acetic acid.

In the degradation of PVA, the production of ketene and the other non-condensable products occurs as low as 300°C, but the reaction conditions of a highly viscous molten polymer are very different from the flow conditions used in the studies of acetic acid decomposition. It is possible that the "residence time" of the acid in the molten polymer is longer and the contact more intimate than in the studies outlined above, but it is extremely difficult to attempt to simulate the experimental conditions prevailing during PVA degradation for the decomposition of acetic acid, and it may even be possible that the reaction is catalysed on the surfaces of the degrading polymer matrix. However, it appears that acetic acid decomposes by a molecular mechanism and that the interacting radical is in fact the acetate radical from PVA degradation, although the evidence to support this is limited and the possibility of a radical decomposition of acetic acid cannot be completely excluded.

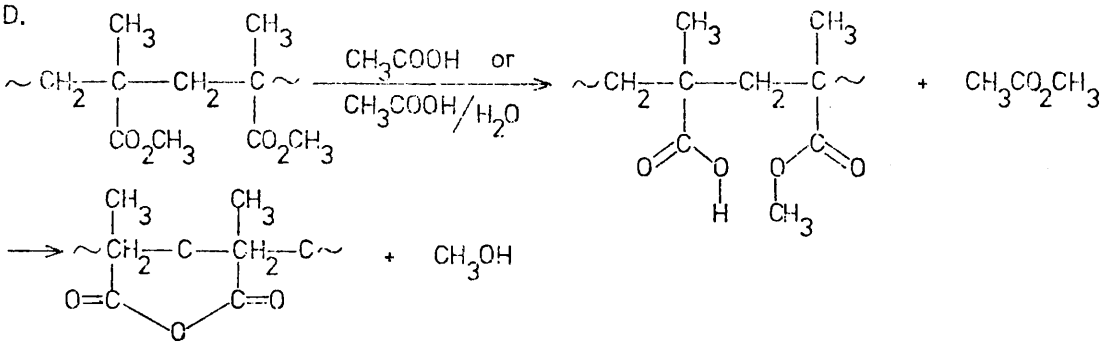
DELAY IN ACETIC ACID PRODUCTION.

If acetate radicals are chain carriers for PVA deacetylation then removal of even a small number of these chain carriers (by the interaction outlined above), may decrease the rate of the reaction. Acting in this respect, PMMA has been compared to a rather inefficient radical scavenger (21).

SUBSEQUENT STABILISATION OF PMMA.

Formation of anhydride rings in the PMMA chain by reaction with acetic acid accounts not only for the stabilisation of PMMA, but for the production of non-condensable material (at higher temperatures) from breakdown of the anhydride structures. The direct formation of these anhydride units in PMMA by reaction with HCl (mechanism A earlier in this chapter) has been favoured (27), but the identification of acid groups in the PVA-PMMA system suggests the possibility of a two-stage reaction. McNeill and Neil (21) proposed such a reaction in which anhydride formation resulted from dehydration of two adjacent methacrylic acid units. However, water was not identified as a reaction product and in any case, the probability of formation of two adjacent methacrylic acid units is extremely small in a reaction which only occurs to a very small degree. On the other hand, it has been shown (chapter eleven) that anhydride ring formation can take place between adjacent methacrylic acid and methyl methacrylate groups in copolymers of these two monomers, with elimination of methanol. Using this information, the suggested reaction pathway for anhydride formation in PMMA from PVA-PMMA blends is shown in (D) below.

D.



This mechanism is supported by the detection of both methanol and methyl acetate amongst the volatile products.

THE MECHANISM OF PVA DEGRADATION.

In the introduction to this chapter, it was stated that a study of the interactions occurring during the degradation of PVA-PMMA blends might provide information about the mechanism of degradation of PVA. The principal points in the vacuum degradation of PVA are :-

(1) The mechanism of deacetylation; free radical or molecular?

(2) The origin of ketene and the other minor products.

(3) Point of initiation of deacetylation; at chain ends or random?

(4) Nature of the termination and cross-linking reactions.

The degradation of the mixed polymer system reveals little about the point of initiation, but it does indicate that a radical process is occurring, which supports the view that a radical deacetylation mechanism, involving acetate radicals, is in operation. Such a reaction means that transfer and combination of free radicals could lead to cross-linking and termination. Ketene and the other minor products probably arise from decomposition of acetic acid by a molecular mechanism, although the molten polymer environment may alter the mechanism. The nature of PVA deacetylation will be discussed further in later chapters.

SUMMARY

Studies have been made on the thermal degradation of PVA-PMMA blends, and it has been found that PMMA can be destabilised by acetate radicals from degrading PVA. Subsequent stabilisation of PMMA results from the production of anhydride units in the polymer chain.

CHAPTER FOUR

THE THERMAL DEGRADATION OF POLY(VINYL ACETATE) - POLY(VINYL CHLORIDE) BLENDS.

Poly (vinyl acetate) and poly (vinyl chloride) exhibit similar degradation behaviour in that they both degrade by an elimination reaction which produces a residue containing conjugated double bonds, and yields the corresponding acids, acetic acid and hydrogen chloride respectively. PVC, which is less stable than, and has longer polyene sequences than PVA (36) yields HCl as elimination product, while PVA produces a small amount of volatile products simultaneously with acetic acid. Because of the similarity of their degradation and also of their behaviour during degradation as blends with poly (methyl methacrylate), PVA and PVC mixtures make an interesting system for investigation.

INTRODUCTION.

Geddes (8) has comprehensively reviewed the thermal degradation of PVC, and so the following discussion will be limited to three principal topics and recent developments in this field. The three subjects are :-

(1) Sites of initiation for thermal degradation.

(2) The mechanism of dehydrochlorination.

(3) The effect of HCl on the rate of dehydrochlorination.

(1) INITIAL SITES OF DEHYDROCHLORINATION.

From "model" investigations with 2, 4 - dichloro-alkanes, it might be expected that the hypothetical structure of PVC, $(-CH_2-CHCl-)_n$, should not lose HCl at temperatures below 300°C (54), and thus various structural irregularities have been discussed as initiation sites of dehydrochlorination.

Branch points in PVC, giving tertiary carbon-chlorine bonds have been postulated as labile sites in PVC, but neither Guyot (55) nor Braun (56) found any relationship between the number of branch points and the rate of dehydrochlorination.

End groups can be formed from initiator residues by chain transfer termination, and although different rates of dehydrochlorination have been obtained for PVC prepared with various initiators, the results of these investigations must be interpreted with caution since the molecular weights of the samples are not comparable, and also because there is no information on other structural irregularities (8, 56). However, it should be mentioned that some workers (57, 58) have observed a correlation between the rate of dehydrochlorination and the inverse of molecular weight (which in turn is proportional to the concentration of chain ends).

Geddes (59) has recently shown that hydroperoxide groups deliberately introduced into PVC are a source of instability, probably behaving as initiators for a radical chain dehydrochlorination, but no positive proof exists to suggest that such groups are formed under normal conditions in PVC. Other irregularities, such as head-to-head units, and the presence of extraneous impurities have been proposed as causing initiation, but again no definite proof exists to confirm these propositions (8).

Finally, it should be mentioned that up to now there is not enough information about the influence of the stereoregularity of PVC on its thermal behaviour. It appears that with an increasing number of syndiotactic links, the thermal stability increases, but this can also be due to the higher crystallinity and the higher melting temperatures of these samples (56).

MECHANISMS OF DEHYDROCHLORINATION

The radical mechanism, as proposed by Stromberg (60) is shown below :-

Initiation $PVC \longrightarrow Cl\cdot$

Propagation

$Cl\cdot + \sim CH_2-CHCl-CH_2-CHCl-CH_2-CHCl-CH_2-CHCl\sim$

$HCl + \sim\dot{C}H-CHCl-CH_2-CHCl-CH_2-CHCl\sim$

$Cl\cdot + \sim CH=CH-CH_2-CHCl-CH_2-CHCl\sim$

$HCl + \sim CH=CH-\dot{C}H-CHCl-CH_2-CHCl\sim$

$Cl\cdot + \sim CH=CH-CH=CH-CH_2-CHCl\sim$

Termination

$Cl\cdot + Cl\cdot \longrightarrow Cl_2$ (a)

$R_1\cdot + R_2\cdot \longrightarrow R_1 + R_2$ or $R_1\ R_2$ (b)

$R\cdot + Cl\cdot \longrightarrow RCl$ (c)

where R = polymer radical and R = polymer molecule. Assuming termination was mainly reaction (a) Stromberg accounted for the $^3/_2$ order he obtained, but chlorine has never been detected in the volatile products, possibly owing to its great reactivity.

Marks et al (61) are among the most recent authors to suggest that PVC degrades by an ionic mechanism, involving the propagation step :-

$$-CH=CH-CHCl-CH_2- \longrightarrow -CH=CH-\overset{\oplus}{C}H-CH_2-$$

$$Cl^{\ominus}$$

$$\longrightarrow -CH=CH-CH=CH- + HCl$$

These workers base their argument on the nature of the reaction between PVC and stabilisers of the type $R_2\ Sn\ Y_2$, which they believe proceeds by an ionic mechanism of the Friedel-Crafts type. They also indicate that the dielectric constant of PVC at degradation

temperatures may be sufficiently high to support the charge separation process necessary for ionic intermediates so formed. The catalytic effect of HCl on the process is, they propose, a result of the known ability of HCl to catalyse carbonium ion reactions.

According to the molecular mechanism for dehydrochlorination, HCl is liberated from the polymer by a concerted reaction, without the intermediate formation of either radical or ionic species. The initiation step in this process is visualised as being the loss of HCl from a labile centre in the molecule, and then allylic activation of the neighbouring hydrogen atom promotes the loss of a further molecule of HCl, giving rise to the observed "zipper" characteristic of the process.

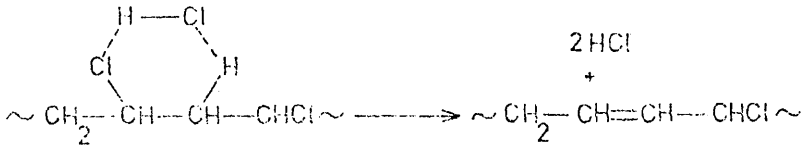
$$- CH = CH - CH_2 - CHCl \xrightarrow{-HCl} - CH = CH - CH = CH -$$

In essence a molecular mechanism is equivalent to an ionic or radical process in which $Cl^{\ominus}$ or $Cl^{\cdot}$ does not become fully detached from the PVC molecule, and tends to attack the neighbouring hydrogen preferentially rather than migrating to another polymer chain.

A great deal of circumstantial, rather than conclusive evidence has been gathered to support the different mechanisms and this has recently been summarised by Braun and his co-workers (56, 62).

Influence of HCl on Dehydrochlorination.

Catalytic acceleration of degradation of PVC by HCl has been observed both for solid samples (63) and in PVC degraded in solution (62). Braun and Bender (62) consider that the autocatalytic effect of HCl cannot be explained by a radical mechanism and they have proposed a non-radical interaction as follows :-



Razuvaev et al (63) on the other hand, consider the accelerating effect of HCl is connected with its interaction with the polyene units via a radical mechanism. Thus, although the mechanism of the catalysis reaction is not clear, the accelerating effect of HCl is beyond doubt.

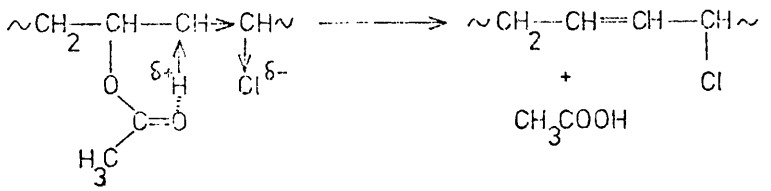
The Degradation of (Vinyl Acetate)-(Vinyl Chloride) Copolymers.

While the degradation of PVA was discussed at some length in the previous chapter and needs no further comment at this stage, it is appropriate to consider the degradation of the copolymer system corresponding to the blend under investigation.

Grassie et al (64, 65) studied the thermal decomposition of (vinyl acetate) - (vinyl chloride) copolymers, both in bulk and in solution. Bulk degradation revealed that at each extreme of the composition range, incorporation of the co-monomer unit resulted in a copolymer less stable than the homopolymer, with a minimum of stability at a composition of 40-50% VA. In solution degradation this minimum of stability occurred at about 30-40% in the copolymer, and in both cases the proportion of acetic acid and HCl produced from the copolymers was constant during degradation, indicating that neither acid was evolved preferentially once reaction had begun.

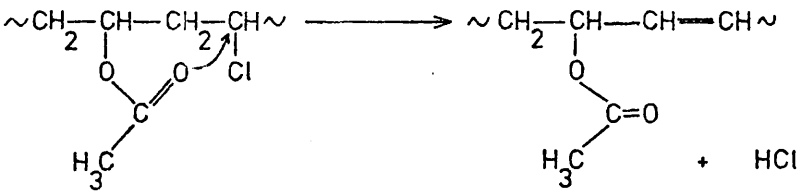
It was concluded by these workers (64, 65) that both the overall rate and the development of conjugation by progression of the reaction along the chain, are increased considerably by some heterogeneity of the chain units, leading to a labilising effect on one or both units by the immediate proximity of a unit of the opposite type. Two mechanisms were proposed that might contribute to this behaviour.

Firstly, the inductive effect of the chlorine atoms may weaken the C-H bonds of the methylene group and so facilitate elimination of acetic acid :-



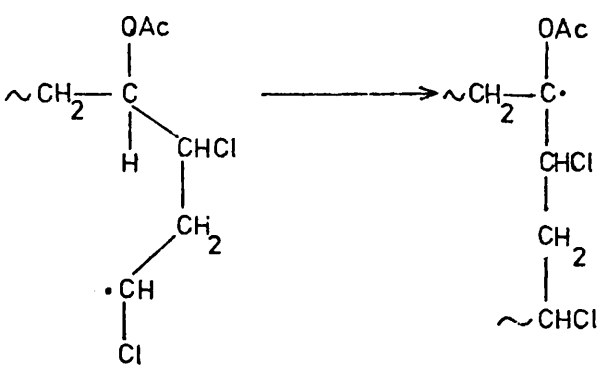
The next molecule to be eliminated will be HCl because of allylic activation.

Secondly, there may be neighbouring group participation by the acetate group in the elimination of HCl :-



There is now allylic activation for removal of an acetic acid molecule.

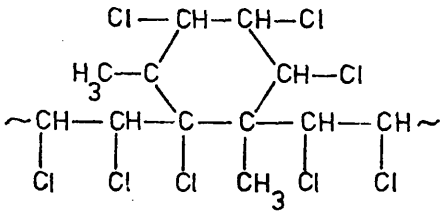
However, it is also possible that an increase in the number of initiation sites in the copolymers could lead to an increased rate of degradation. These labile structures may be chain branches which result, during copolymerization from intra-molecular transfer reactions. Guyot (66) has observed transfer during copolymerization of VA and VC, and has suggested that this may arise via the following novel reaction :-



POLYMERS USED

The PVA samples listed in Table (3.1) were again used in this work. Two different PVC samples were used: PVC Breon 113 (Mn 64,500) was the most extensively used sample and was a British Geon, additive-free polymer, purified by precipitation (twice) in methanol from cyclohexanone solution, and dried under vacuum for several days at room temperature. A PVC sample, PVC RA, prepared from vinyl chloride containing Cl-36 was kindly donated by Dr. B. Dodson. The polymer had been polymerised in bulk at 40°C using 0.2% AIBN as initiator and purified as above.

Alloprene is a chlorinated natural rubber containing 64.5% by weight fixed chlorine, and was obtained from I.C.I. Ltd. The structure described by the company is a straight carbon chain containing a small unspecified number of ring structures, shown below:-



The sample employed in this work was a 20 c.p. grade and the number-average molecular weight 64,700.

Poly (vinylidene chloride) was prepared by Dr. R. McGuchan in bulk at 40°C using 0.05% AIBN as initiator.

The sample of polychloroprene used was Butachlor MC 30 (Distillers Co. Ltd.), a mercaptan modified emulsion polymer, re-precipitated twice from toluene into methanol under nitrogen. Solutions of this polymer were stored under nitrogen in the dark to minimise oxidation effects.

RESULTS AND DISCUSSION.

This section will deal with the PVA - PVC system, other blends systems being dealt with at the end of the chapter.

THERMAL VOLATILIZATION ANALYSIS.

For the most part, the blends were examined as films cast from solution of the mixed polymers in cyclohexanone or tetrahydrofuran. The sample sizes were 30 mg for each polymer except for experiments using different ratios of polymers and the heating rate was 5 ^{o}C/min.

The TVA trace for a PVA film is shown in figure (4.1), and apart from the peak for deacetylation being slightly broader, as expected for degradation carried out at a slower heating rate and same chart speed, it is identical in all other respects to the TVA trace for PVA at 10^{o}C/min discussed in chapter three. The TVA behaviour of film and powder samples of PVC is shown in figure (4.2). In both cases the first part of the volatilization is composed of material non-condensable at -100^{o}C (HCl), and hence the traces for the 0^{o}, -45^{o}, -75^{o} and -100^{o} traps are coincident. The complex shape of this first part of the TVA curves has been attributed by McNeill and Neil (20) to the effect of catalysis by HCl diffusing through the sample, and it can be seen from figure (4.2) that there is a slight difference in the volatilization behaviour of the powder and film samples, although the traces are qualitatively similar. The high temperature peak above 400^{o}C results from products, a large proportion of which are non-condensable at -196^{o}C, and this volatilization is due to breakdown of the polyene residue resulting from dehydrochlorination.

TVA traces for equal amounts of PVA and PVC degraded simultaneously as unmixed and mixed films cast from cyclohexanone, are shown in figure (4.3). In the trace for the unmixed samples, the large

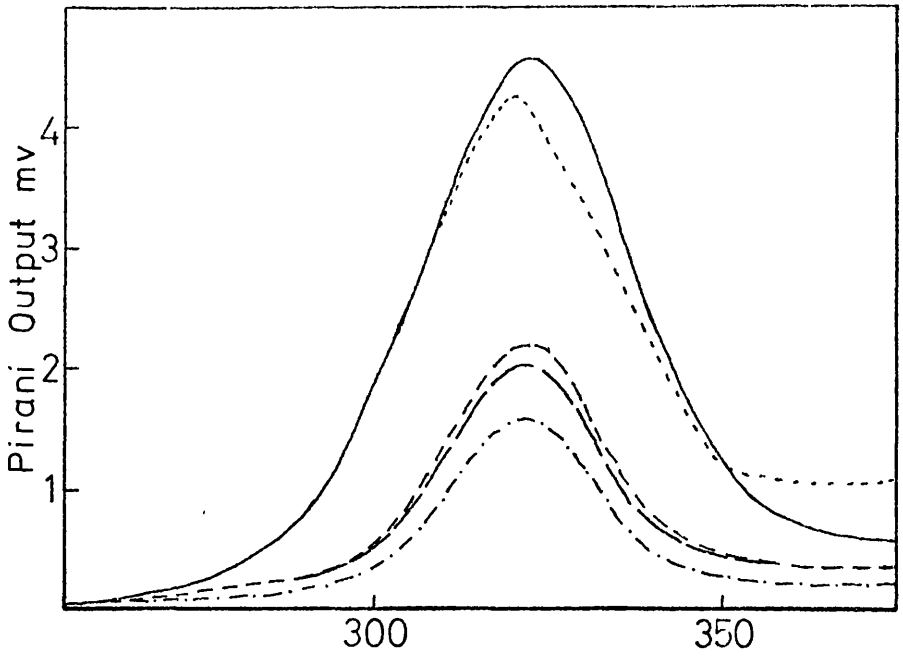


Figure (4.1). TVA curve for PVA (BDH). Sample as 50 mg film. Heating rate 5°C/min.

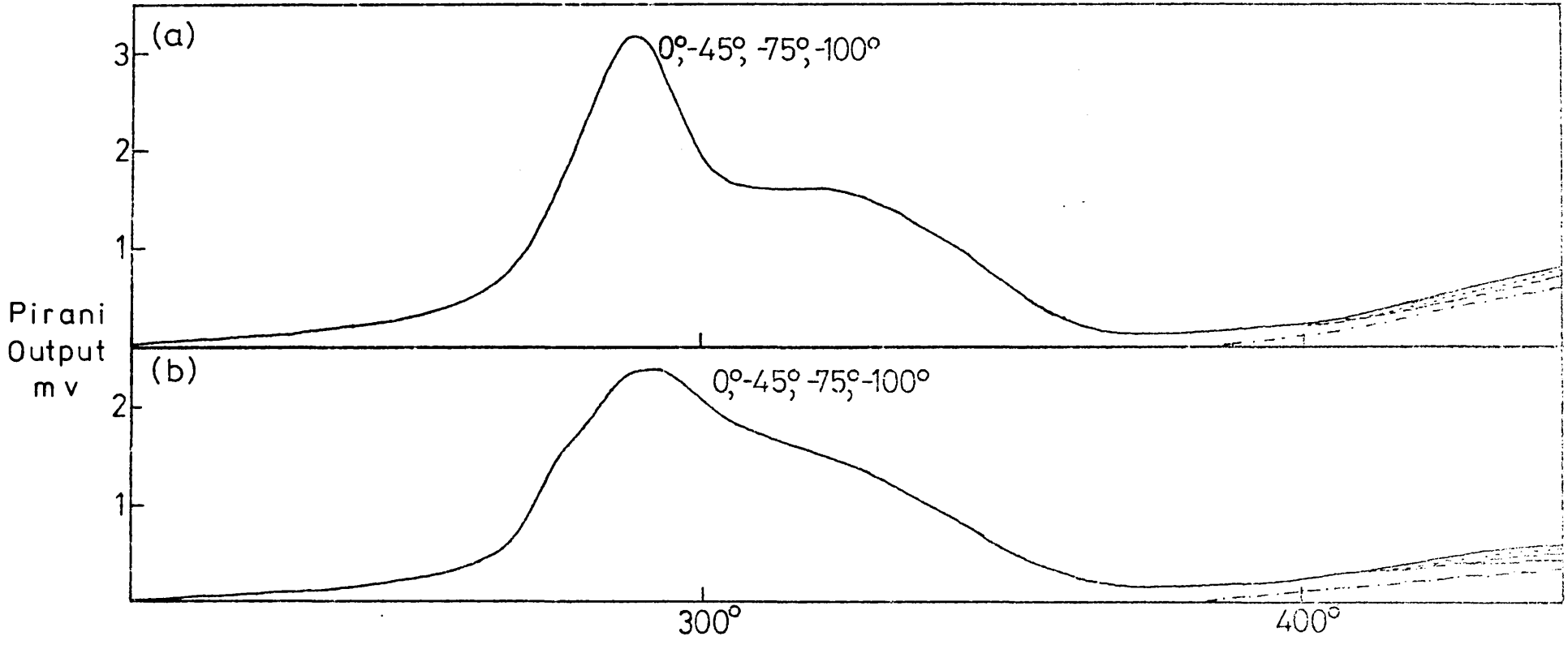


Figure (4.2). TVA Curves for PVC Breon 113. 50 mg samples, (a) powder (b) film. Heating Rate 5°C/min.

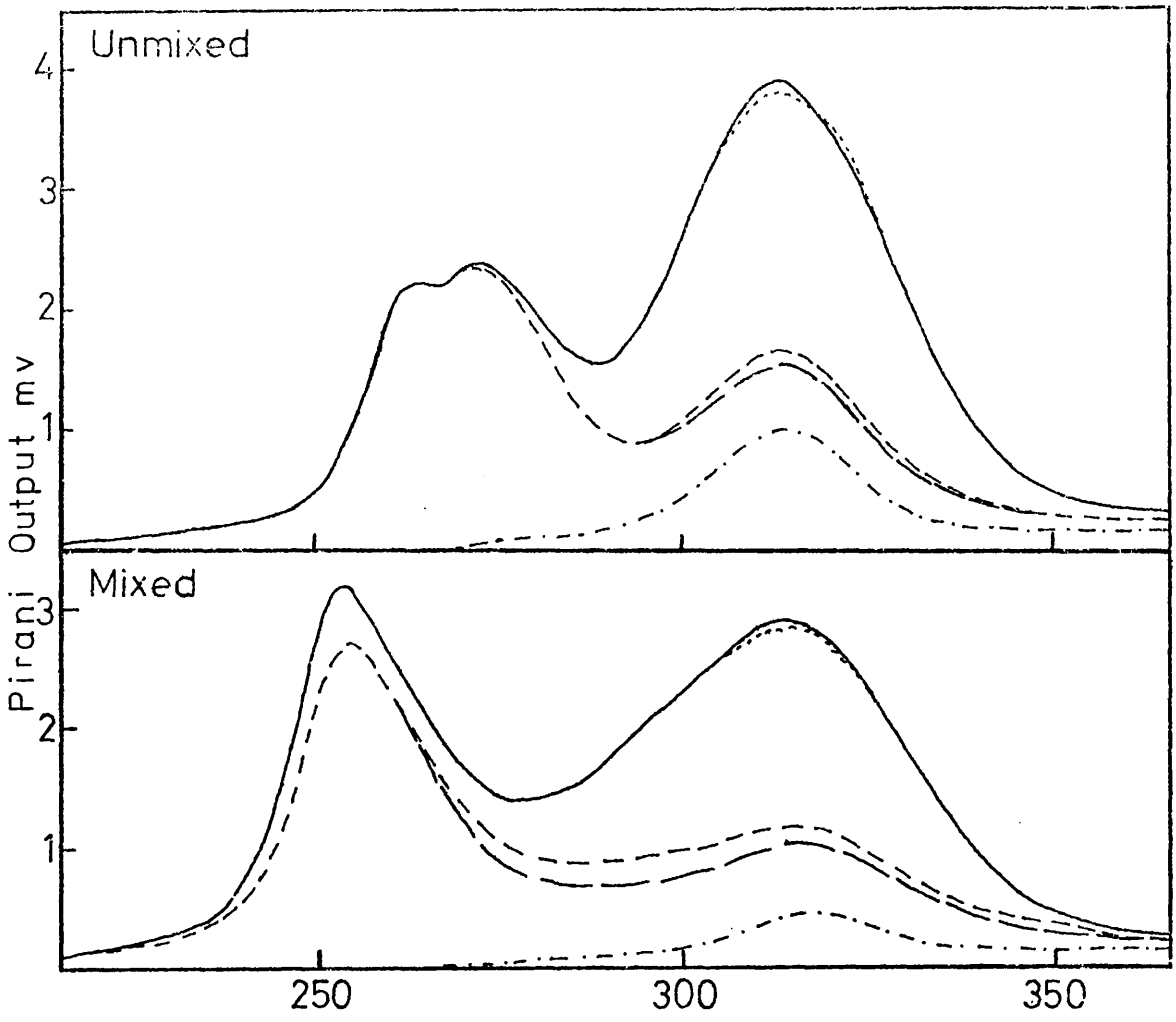


Figure (4.3). TVA curves for equal amounts of PVA (BDH) and PVC Breon 113 (30 mg of each polymer), degraded as unmixed and mixed films at 5°C/min.

Solvent cyclohexanone.

peak above 300°C is that for deacetylation of PVA, while the smaller "double" peak below 300°C is due mainly to PVC. The "first half" of this latter peak is solely material which is non-condensable at -100°C (i.e. HCl from PVC) while the "second half" results from the overlap of dehydrochlorination with the initial stages of deacetylation, shown by the condensability of material at -75°C and the production of material non-condensable at -196°C.

The trace for the mixed sample shows an increased rate of volatilization at low temperatures compared with the unmixed sample. Although the peak around 257°C is for the most part, due to material non-condensable at -100°C (i.e. HCl from PVC), there is material which is condensed at -75°C evolved at this stage too. This suggests acetic acid production from PVA is occurring at temperatures as low as 230°C compared with 270°C for unmixed samples. Also the production of HCl (-100°C trace) appears to be occurring at a faster rate. The peak at higher temperatures has the same temperature of maximum volatilization rate (T max) as the unmixed sample, but the peak height is smaller, presumably for two reasons. Firstly, less acetic acid is being evolved at this stage, since the deacetylation is occurring earlier and hence over a wider range of temperatures. Secondly, the production of material non-condensable at -196°C, which accompanies PVA deacetylation, is also reduced in amount in the mixed sample, although the temperature at which this material first appears is the same for both samples (~270°C).

The effect of varying the ratio of the polymers is shown in figure (4.4) for a 5:1 mixture by weight of PVA : PVC. For the unmixed system, the volatilization of HCl is observed merely as a shoulder on the low temperature side of the PVA deacetylation peak. Again, for the mixed sample there is increased volatilization of

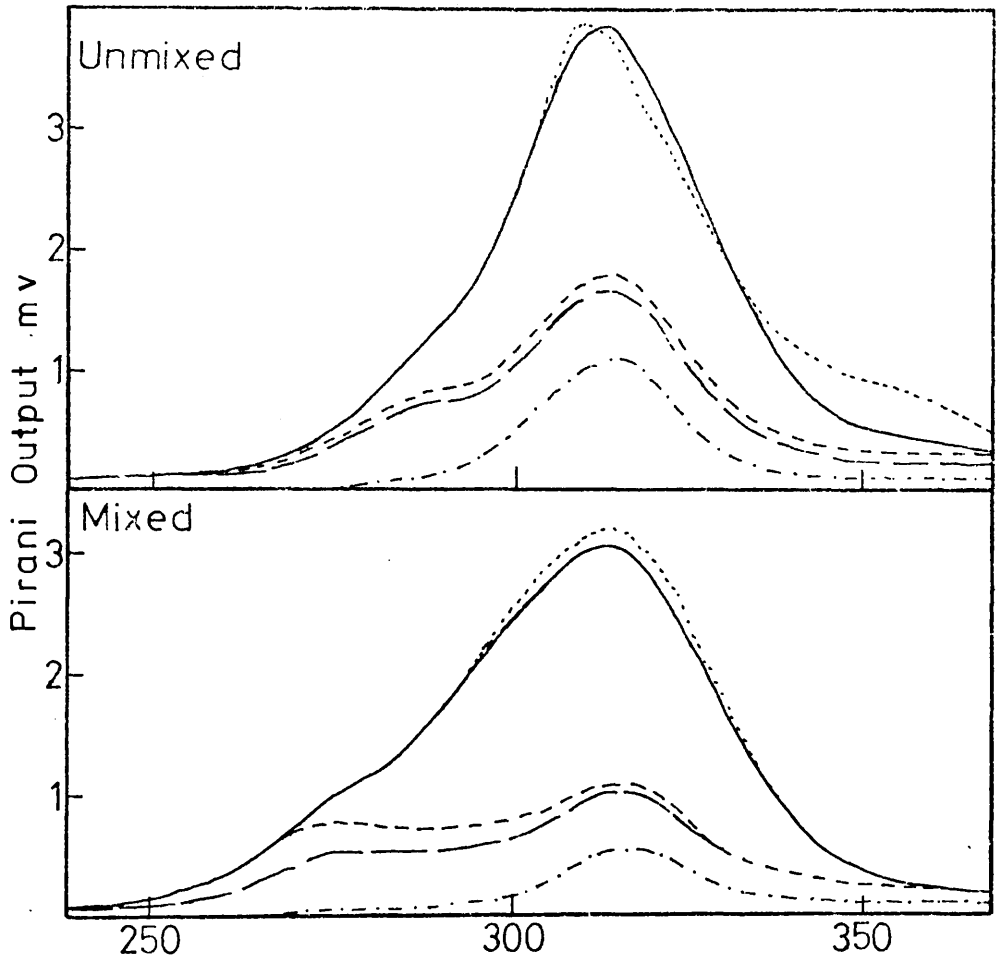


Figure (4.4). TVA Curves for PVA (BDH) and PVC Breon 113, 5:1 by weight respectively (36 mg total weight), degraded as unmixed and mixed films at 5°C/min.
Solvent cyclohexanone.

of both acetic acid and HCl at low temperatures, a broadening and reduction in height of the PVA peak and production of a smaller amount of material non-condensable at -196°C. Qualitatively these effects are similar to these observed for the 1:1 by weight system.

Similar effects are obtained from mixed and unmixed films cast from tetrahydrofuran (figure (4.5)), and also from mixed and unmixed powder systems (figure (4.6)), although the differences between the mixed and unmixed powders are smaller than for the film samples. Also, using different samples of PVA and PVC the same qualitative interactions were observed.

THERMOGRAVIMETRIC ANALYSIS.

TG analysis of PVA and PVC powders was carried out under a dynamic nitrogen atmosphere at 5°C/min. The similarities in the weight loss behaviour of these two polymers are illustrated in figure (4.7). Weight loss occurs in two stages for both polymers, the first stage corresponding to volatilization of acetic acid and HCl respectively while the second corresponds to decomposition of the conjugated polyene residues. The final residue at 500°C is greater for PVC than for PVA.

The curve obtained from degradation of a mixture of equal weights of PVA and PVC is shown in figure (4.7), with the "theoretical" curve obtained by addition of the traces for PVA and PVC. It can be seen that the observed curve loses weight more rapidly than the expected curve in the temperature range 250°C to 400°C, in the region of weight loss due to dehydrochlorination and deacetylation. Above 400°C in the temperature region of decomposition of the polyene chains, the weight loss observed for the mixture is similar to the expected weight loss behaviour.

INFRA-RED ANALYSIS OF VOLATILE PRODUCTS

IR analyses were made of volatiles from vacuum degradation (90 minutes at 380°C) of mixed and unmixed films of PVA and PVC. The sample sizes were 50 mg of each polymer and the products were fractionated at -80°C, the products non-condensable at -196°C being collected by degradation in a closed system. The results of these analyses are listed in Table (4.1)and the spectrum of a fraction, from a mixed system, non-condensable at -80°C, but condensed at -196°C, is shown in figure (4.8).

The characteristic band spectrum of HCl is evident in the region 3050-2600 cm^{-1} ; carbon dioxide may be recognised by its absorptions at 2320-2345 cm^{-1} and below 700 cm^{-1} ; while acetyl chloride has absorptions at 1828 and 1810 cm^{-1} (C=O stretching vibrations) and around 1100 cm^{-1} (C-O stretching vibration).

From Table (4.1) it may be seen that the only product which is not obtained from degradation of the homopolymers is acetyl chloride. Acetyl chloride was not detected from degradation of unmixed samples of PVA and PVC, but was observed in the degradation products of a (vinyl acetate) - (vinyl chloride) copolymer containing 75% vinyl acetate. Thus it would appear that formation of acetyl chloride takes place in the reaction zone and not in the cold traps.

TABLE (4.1)

Voltatile products of degradation of PVA - PVC blends, observed by I.R.

Condensable at -80°C	Non-condensable at -80°C	Non-condensable at -196°C
Acetic Acid Water (trace)	Hydrogen Chloride Acetyl Chloride (trace) Carbon Dioxide (trace)	Carbon Monoxide (trace) Methane (trace)

Ketene, which is obtained from degradation of PVA, was not detected from the mixed system degradations. This fact may be connected with

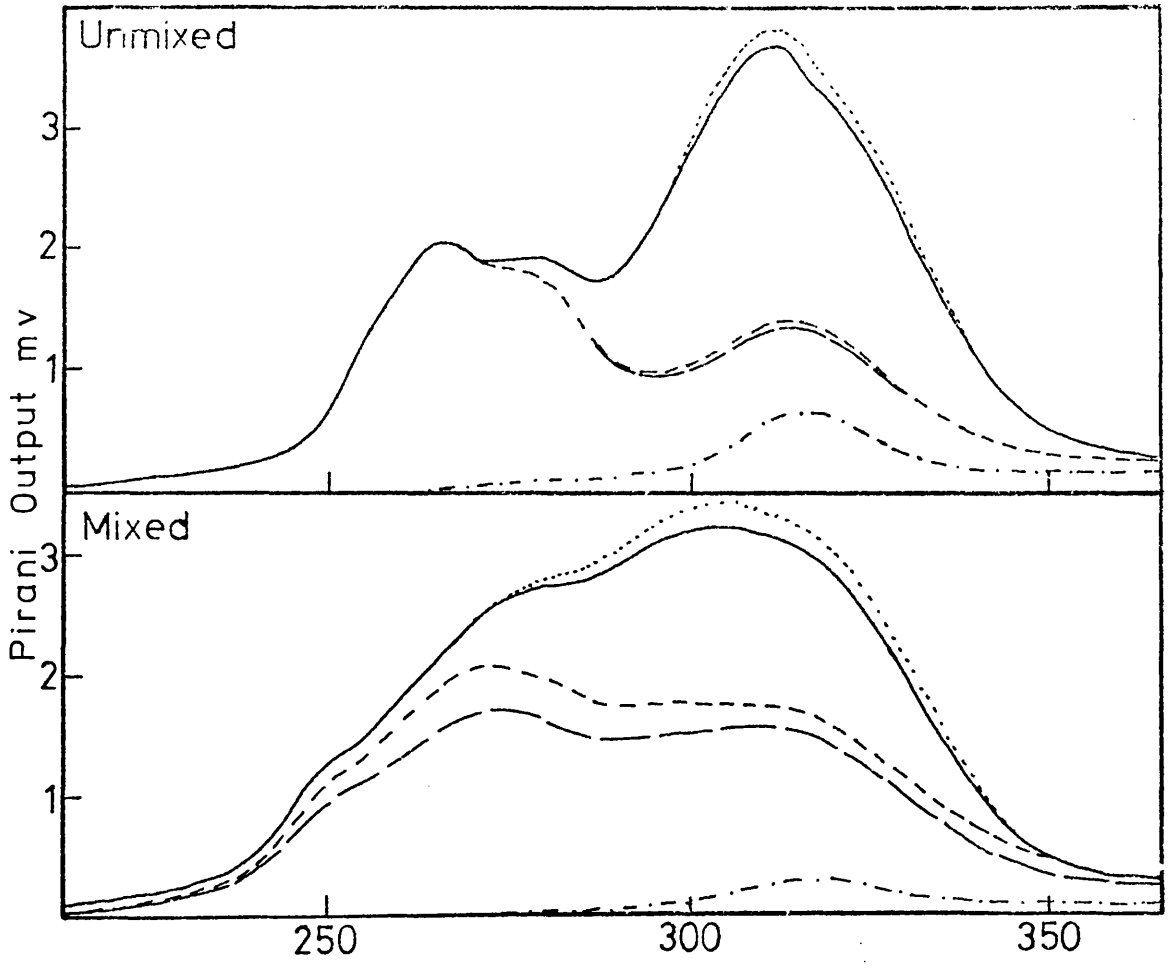


Figure (4.5). TVA curves for equal amounts of PVA (BDH) and PVC. Breon 113 (30 mg of each polymer), degraded as unmixed and mixed films at 5°C/min.

Solvent tetrahydrofuran.

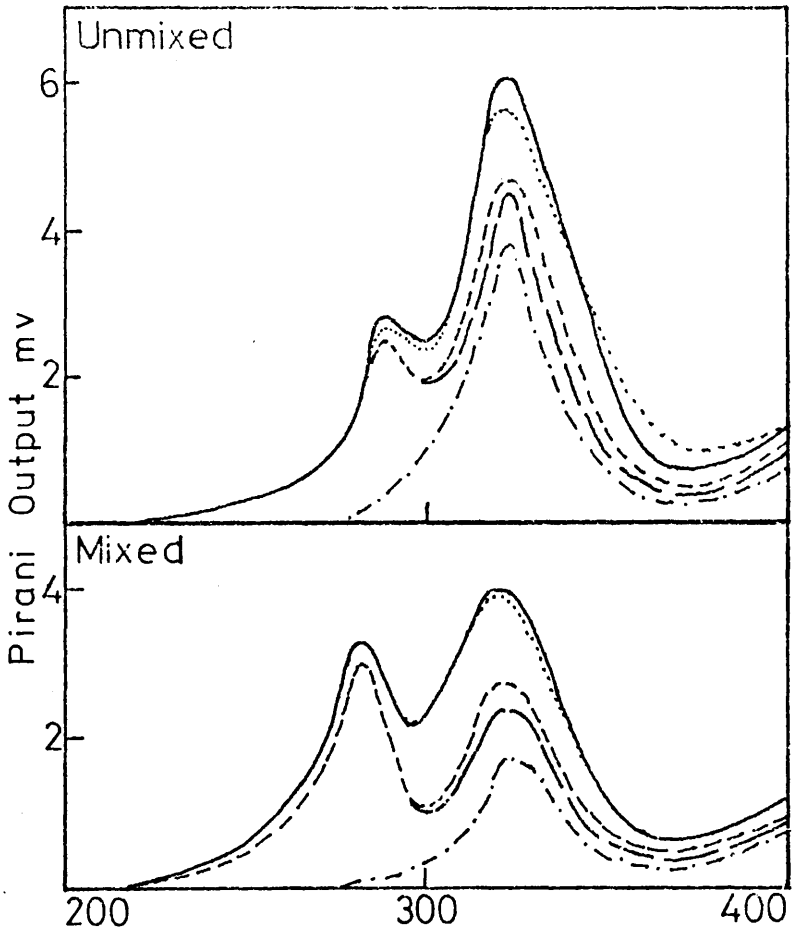


Figure (4.6). TVA Curves for equal amounts of PVA (BDH) and PVC Breon (40 mg of each polymer), degraded as powders at 5°C/min.

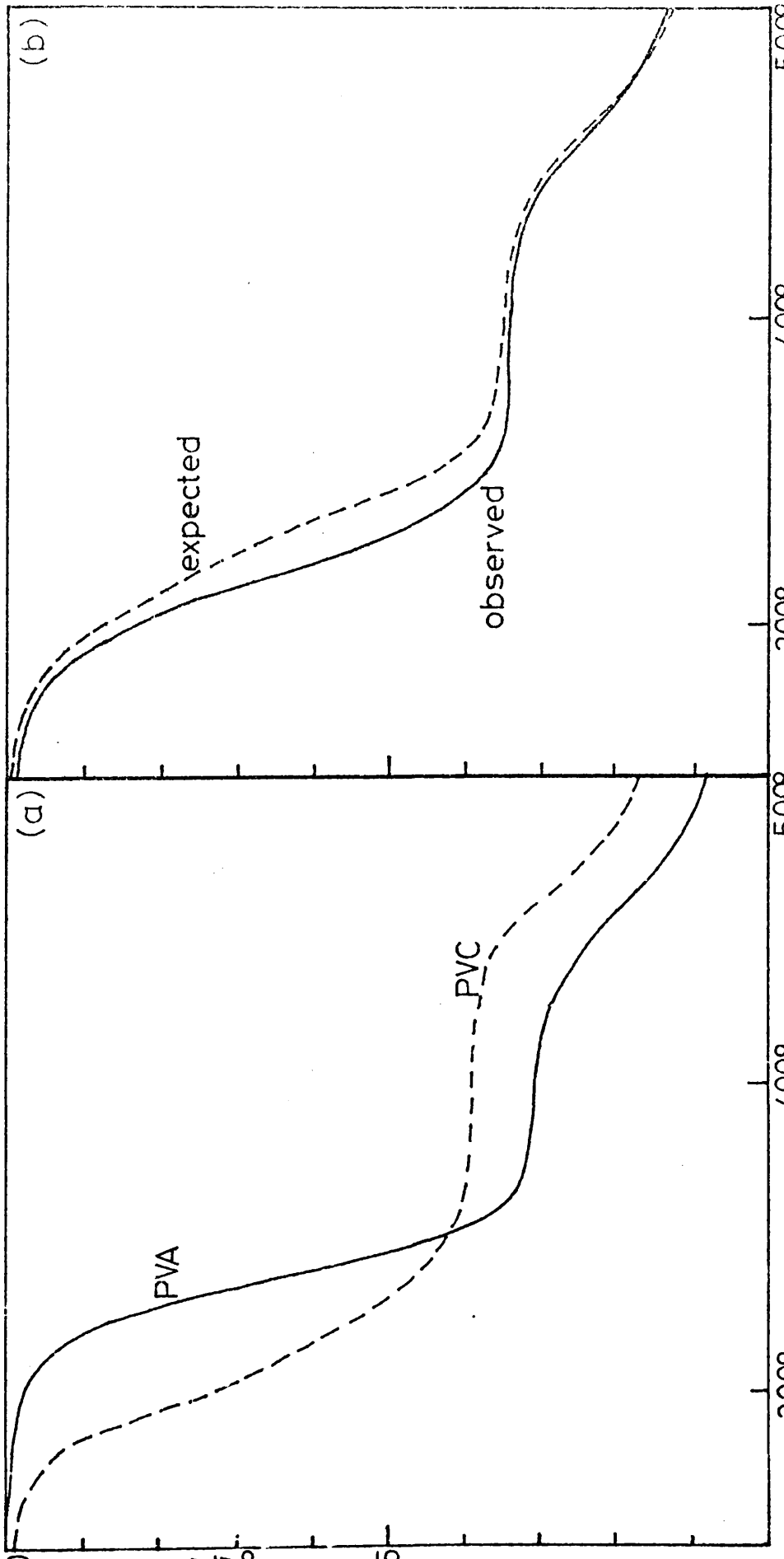


Figure (4.7). (a) TG curves for PVA (BDH) and PVC Breon 113.
(b) Comparison of "expected" and observed TG curves for a 1:1 mixture of PVA (BDH) and PVC Breon 113.
Samples as 10 mg powders, degraded at 5°C/min under dynamic N_2 flow.

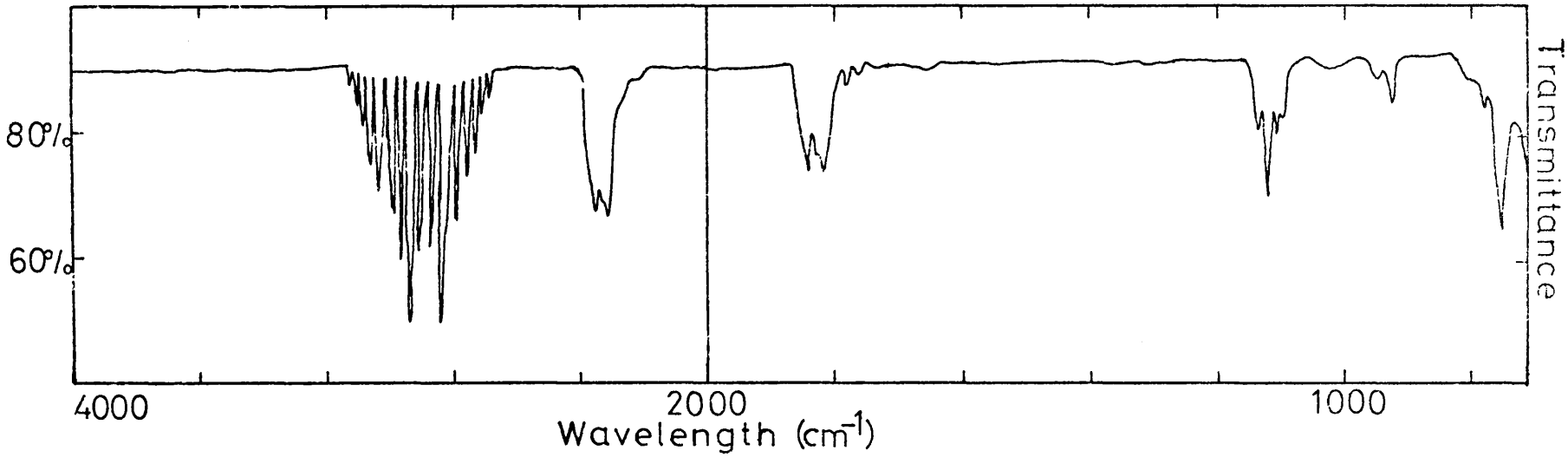


Figure (4.8). Infra-red spectrum of the products of degradation (non-condensable at -80°C) of a PVA (BDH) - PVC Breon 113 (1:1 by weight) mixed film (100 mg), degraded at 380°C for 90 minutes.

the appearance of acetyl chloride, since there are two possible routes of formation of acetyl chloride which involve interaction of the products, including ketene :-

(1) $HCl + CH_3COOH \longrightarrow CH_3CO\,Cl + H_2O$

(2) $HCl + CH_2 = C = O \longrightarrow CH_3CO\,Cl$

It is conceivable that the lack of ketene amongst the degradation products provides evidence for route (2), but route (1) cannot be entirely excluded.

ESTIMATION OF HCl and ACETIC ACID PRODUCTION.

PVA (BDH) and PVC Breon 113 samples (50 mg films) were degraded separately under vacuum at 220°C for periods up to seven hours, and the volatiles produced condensed in water at -196°C. Acetic acid was titrated with standard 0.01 N sodium hydroxide using phenolphthalein as indicator; HCl was estimated by the same technique and also by titration with standard 0.01 N silver nitrate solution using potassium chromate as indicator. Mixed 100 mg (total), film samples of PVA and PVC (equal weights) were degraded under similar conditions and the acids collected as before. The solution containing HCl and acetic acid was titrated with sodium hydroxide to estimate the total amount of acid present, and then with silver nitrate to calculate the amount of HCl collected. The quantity of acetic acid was calculated by difference, and the results of this investigation are shown in figure (4.9) where quantities of acid evolved are presented in terms of the amount of sodium hydroxide required for neutralization. (100% dehydrochlorination from 50 mg PVC requires .58 ml of base).

It can be seen from figure (4.9) that PVC degraded at 220°C has undergone approximately 42% dehydrochlorination after 7 hours, while PVA has undergone about 35% deacetylation after similar treatment.

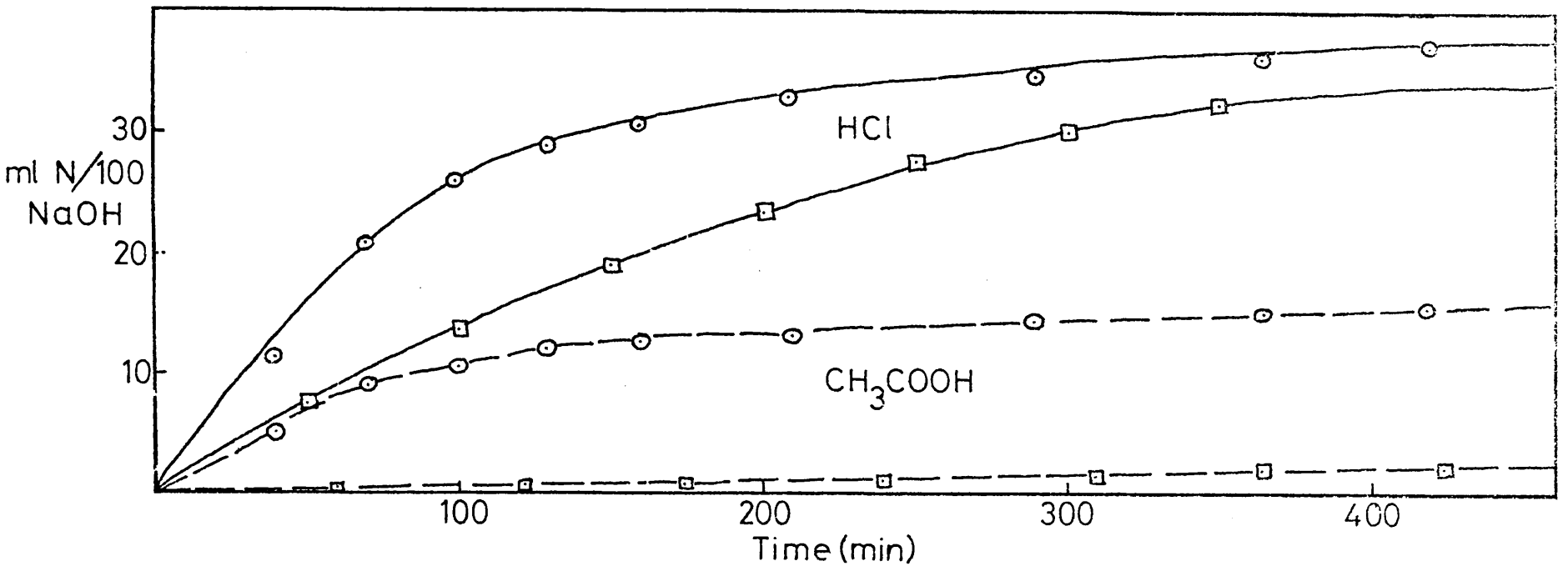


Figure (4.9). Estimation of acids from PVA(BDH), and PVC Breon 113 and 1:1 mixtures by weight of these polymers degraded under vacuum at 220°C.

Key

HCl from PVC

HCl from PVA-PVC mixture.

Acetic acid from PVA

Acetic acid from PVA-PVC mixture.

The production of both acids from the mixed system is more rapid than from the unmixed homopolymers, and indeed 24% deacetylation has occurred after only 100 minutes. The initially more rapid rate of acid production from the mixed system decreases and subsequently occurs at the same rate.

Similar results are obtained from degradation of the PVA - PVC RA system as shown in figure (4.10). In this case the total amount of both acids was estimated as before by titration with standard alkali, and the amount of HCl calculated by radioactive counting along a Geiger-Muller counter, which had previously been calibrated by counting known amounts of HCl from degradation of PVC RA. Again, the rate of production of both acids from the mixed system is initially faster than from the unmixed homopolymers.

These experiments thus confirm the effects observed by TVA, that deacetylation and dehydrochlorination both occur initially at greater rates in blends of PVC and PVA than in unmixed samples. It is known that HCl can catalyse the degradation of PVC (62, 63) and that the rate of dehydrochlorination is initially increased when PVC is degraded in solution with acetic acid (65), but the effect of HCl on PVA degradation has not previously been investigated. Before any discussion of the mechanism of interaction of PVA and PVC during degradation, the effect of HCl on PVA deacetylation will be considered.

EFFECT OF HCl ON THE DEGRADATION OF PVA.

The effect of HCl on the deacetylation of PVA was studied by thermogravimetry, estimation of acetic acid production, and by the production of polyene sequences in the PVA residue using UV spectroscopy.

THERMOGRAVIMETRIC ANALYSIS.

Powdered 10 mg samples of PVA (BDH) were degraded at 5°C/min.,

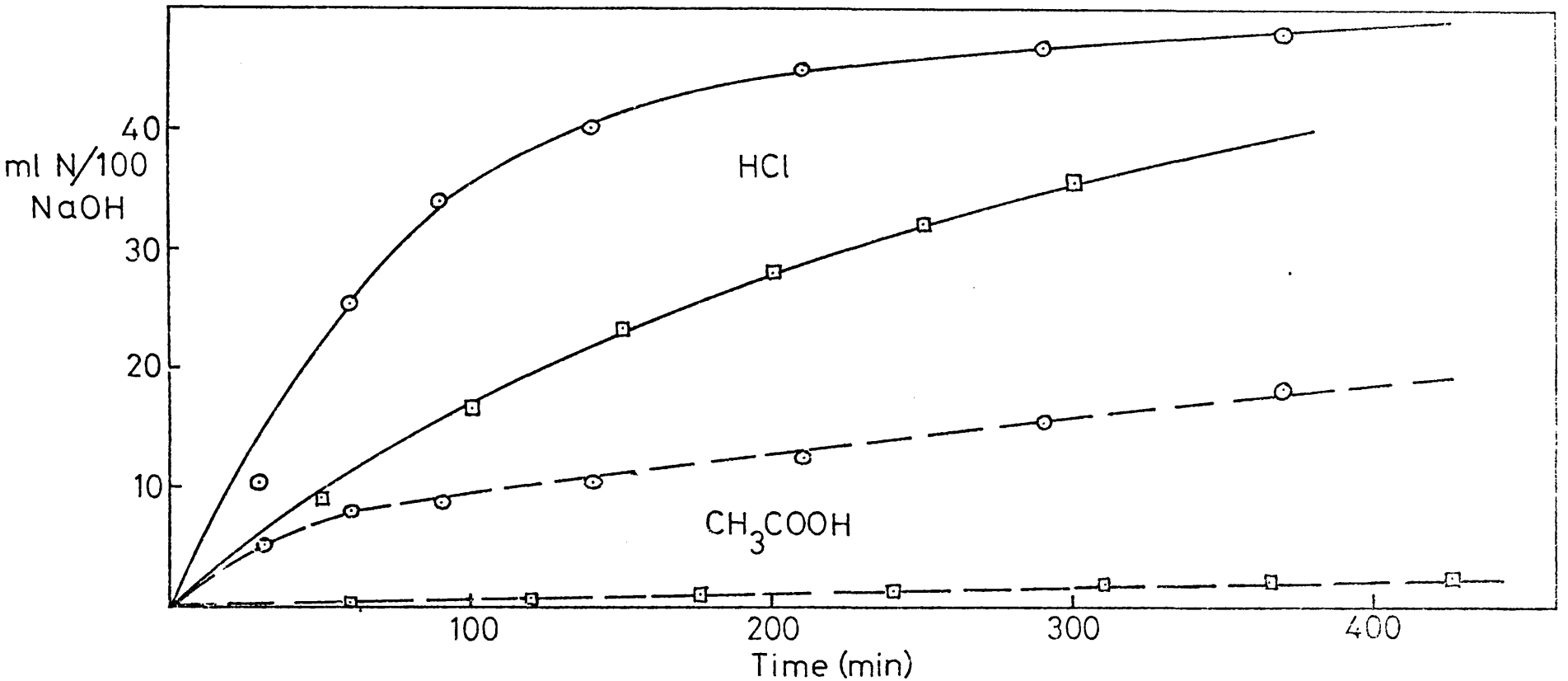


Figure (4.10). Estimation of acids from PVA (BDH), PVC RA, and 1:1 mixtures by weight of these polymers degraded under vacuum at 220°C.

Key

HCl from PVC

HCl from PVA-PVC mixture

Acetic acid from PVA

Acetic acid from PVA-PVC mixture.

(a) in a nitrogen gas flow of 75 ml/min. and (b) in a nitrogen gas flow of 55 ml/min. containing dried HCl flowing at a rate of 20 ml/min. The total gas flow rate was the same for each series of experiments.

The results of these experiments are shown in figure (4.11); the weight loss behaviour for PVA degraded in nitrogen alone being the same as that observed previously in figure (4.7). It can be seen, however, that weight loss from PVA degraded in the presence of HCl occurs at a much greater rate than PVA degraded in a nitrogen atmosphere (28% weight loss compared to 4% weight loss respectively at 300°C). This suggests that deacetylation of PVA is considerably accelerated by the presence of HCl. No formal study was made of the effect of varying the concentration of HCl on the pattern of weight loss, but it was observed that increasing the HCl flow concentration to 27 ml/min., increased the rate of weight loss (to 37% at 300°C).

The residue at 500°C from PVA degraded in HCl was greater than that from PVA degraded under nitrogen alone. The significance of this fact is not immediately apparent, although it may suggest that chlorine has somehow been incorporated in the residue.

ACETIC ACID ESTIMATION.

Twenty mg films of PVA (BDH) were degraded at 265°C in a closed evacuated system for various lengths of time; a liquid nitrogen trap was used to collect acetic acid as it was formed and the acid was titrated against standard base as before. This was repeated, the cold trap being placed in position only at the end of the experiments to collect the acid, thus allowing the effect of acetic acid on the degradation to be observed. It was found that differences in the rate of acetic acid production from both systems were negligible.

Films of PVA were then degraded at the same temperature in the presence of HCl, which had been collected from the degradation of 100 mg

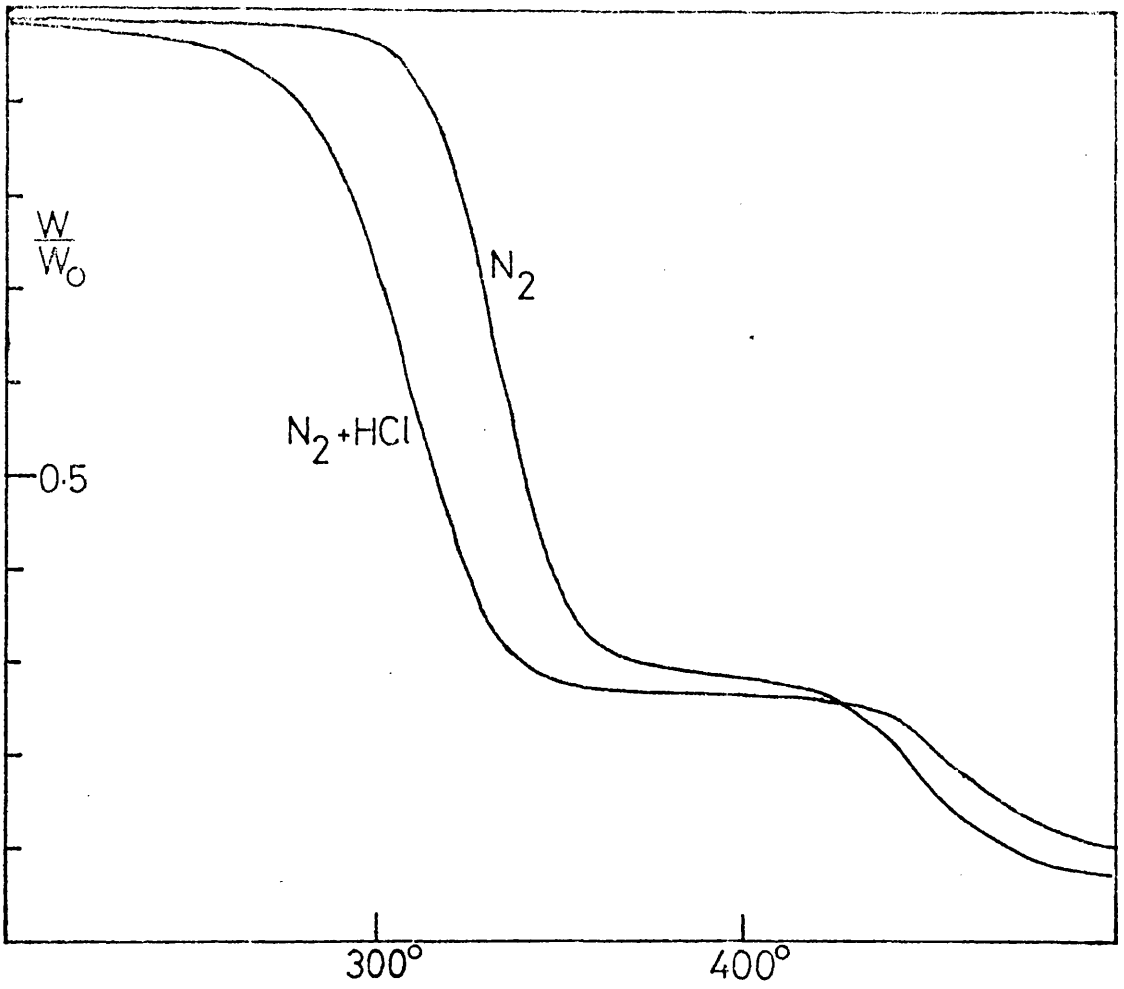


Figure (4.11). TG at 5°C/min of PVA (BDH), 10 mg powder, in nitrogen, and nitrogen containing HCl.

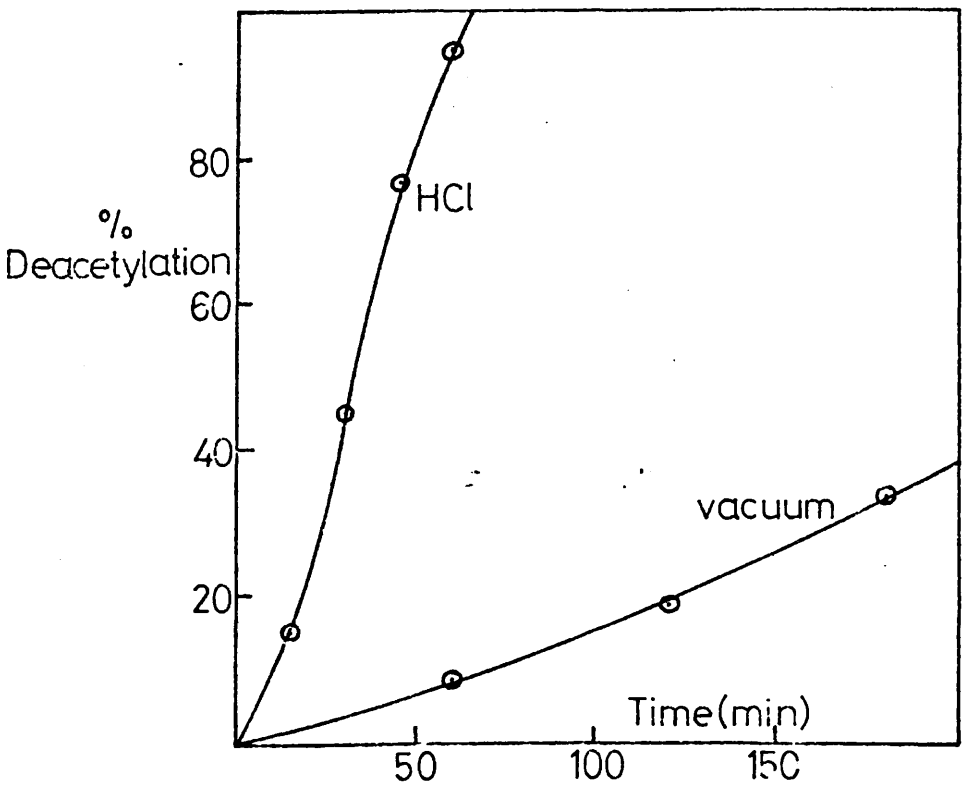


Figure (4.12). Production of acetic acid from PVA (BDH) at 265°C, under vacuum, and in an atmosphere of HCl.

of FVC Freon 113. The degradation system, containing the PVA sample and the HCl condensed in liquid nitrogen, was evacuated and the HCl then expanded into the system. After completion of a particular experiment, the acetic acid was condensed at -80°C, the HCl pumped off, and the acetic acid estimation carried out as before. The results of these experiments are shown in figure (4.12), and it can be seen that degradation of PVA in an atmosphere of HCl accelerates the rate of deacetylation considerably, confirming the weight loss results.

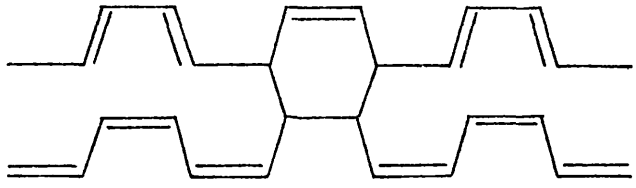
UV STUDIES OF PVA RESIDUE.

It is of interest to observe how the increased rate of deacetylation of PVA, degraded in the presence of HCl, is reflected in the conjugation of the polymer residue, and hence UV spectra of PVA residues were recorded. PVA (BDH) films (20 mg) were degraded at 265°C, (a) under vacuum and (b) in the presence of HCl; the polymer films being cast on a silica TVA degradation tube suitable for direct UV examination of polymer residues.

Spectra for the samples degraded under vacuum for various times are shown in figure (4.13), illustrating the growth of conjugation in PVA residues with increasing extent of deacetylation. It can be seen that absorption does not extend significantly beyond 500 mμ, which corresponds to approximately twelve conjugated double bonds (56), while the short wavelength absorptions grow more rapidly with increasing extents of deacetylation.

For PVA samples degraded in the presence of HCl, it was observed that conjugation built up more rapidly, as expected, since the rate of deacetylation is considerably increased in the presence of HCl. However, the absorption at a particular wavelength (450 mμ) was plotted against the percentage deacetylation as shown in figure

(4.14), for the two systems. For the sample degraded in the presence of HCl, the absorption increases smoothly with increasing extents of deacetylation, while for the vacuum degraded sample the absorption passes through a maximum, decreasing at high percentages of deacetylation. This phenomenon was also observed in VA - VC copolymers (65) and it was suggested that cross-linking of polyene sequences in different chains occurred by a Diels-Alder type reaction to give structures such as



in which long sequences in both chains are interrupted as a result of cross linking. Also, it can be seen that for the same extent of degradation, absorption at longer wavelengths (e.g. 450 m μ) is more pronounced for samples degraded in the presence of HCl, than for samples degraded under vacuum. Thus besides accelerating the rate of deacetylation of PVA, HCl has the effect of producing longer polyene sequences in the PVA residue, than in PVA samples degraded under vacuum. This effect may result from an increase in the chain length of elimination or by a decrease in the amount of cross-linking of the polyenes during degradation of PVA in an atmosphere of HCl.

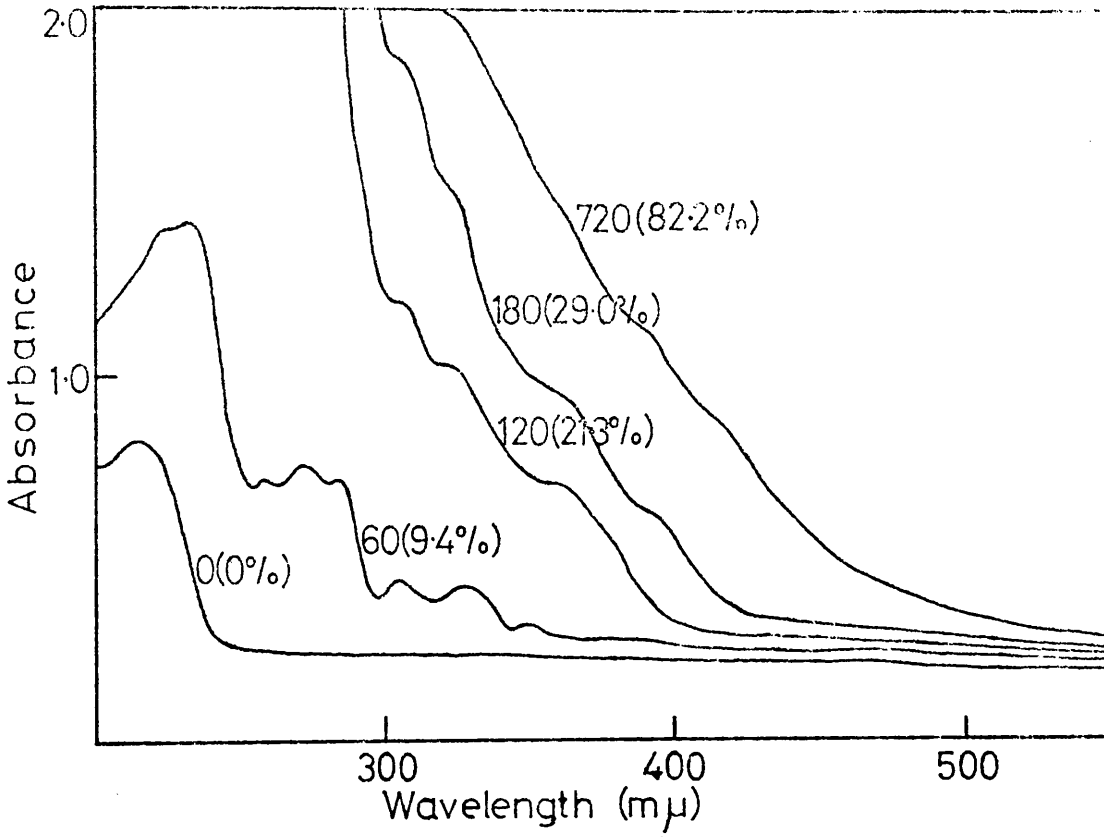


Figure (4.13). U V Spectra for PVA (BDH) degraded under vacuum at 265°C, for different times (in minutes). The percentage deacetylation is given in brackets.

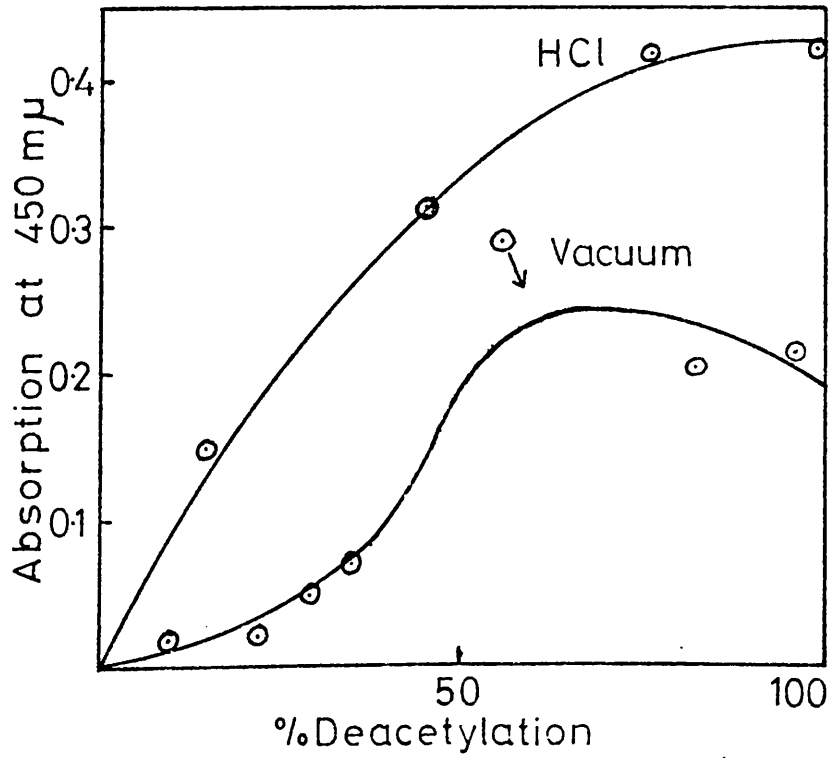


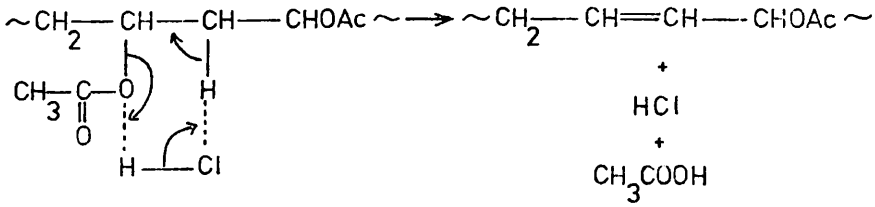
Figure (4.14). U V Absorption at 450 m u versus % Deacetylation for PVA (BDH) degraded at 265°C in vacuum and in an atmosphere of HCl.

DISCUSSION.

During degradation of PVA - PVC blends two principal phenomena occur, viz. the increased rates of deacetylation and of dehydrochlorination of PVA and PVC respectively. For the increased rate of deacetylation, it has been shown that this can be brought about by the presence of HCl during degradation of PVA, but it is also conceivable that chlorine radicals, from degradation of PVC, are responsible for initiating a radical-type deacetylation of PVA. Since the PVA-PVC system is heterogeneous and incompatible, this latter interaction would involve migration of chlorine radicals from PVC domains across phase boundaries. However, acceleration of deacetylation was also observed in mixed powder samples where the less intimate environment makes the interaction involving migration of chlorine radicals less likely. Therefore it is more likely that this acceleration is caused by diffusing HCl interacting with degrading PVA.

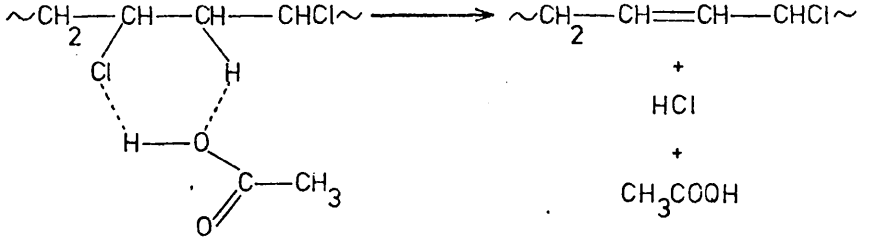
By analogy, the interaction resulting in increased rates of dehydrochlorination of PVC, cannot arise by migration of acetate radicals across phase boundaries, but probably arises from interaction of diffusing acetic acid with degrading PVC.

It is difficult to explain the exact nature of these interactions but it is possible that the accelerating effect of HCl on PVA deacetylation occurs by a mechanism similar to that proposed to explain the autocatalytic effect of HCl on the dehydrochlorination of PVC (62):-

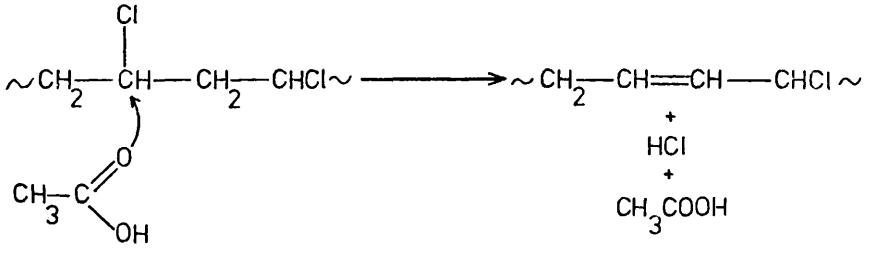


Subsequent deacetylation is now facilitated by allylic activation of acetate units adjacent to the double bonds. In essence, this is similar to the mechanism discussed previously for facilitating acetic acid elimination from VA - VC copolymers (65), involving weakening of the C - H bonds of the methylene group by the intramolecular inductive effect of chlorine atoms.

There are several possible explanations for the interaction of acetic acid with PVC. The first is that it reacts with PVC in a fashion similar to that outlined above for HCl and PVA :-



There is now allylic activation for further dehydrochlorination. The second possible explanation involves a reaction analogous to the neighbouring group participation effect of the acetate group in the elimination of HCl from VA - VC copolymers (65) :-



The third possible explanation is that diffusing acetic acid decomposes via a radical mechanism and that intermediates initiate radical decomposition of PVC. However, catalysis of PVC dehydrochlorination by acetic acid, during degradation in solution at 180°C, was observed by Grassie et al (65), and although no mechanism was proposed for the process, it is doubtful whether radicals would arise from acetic acid decomposition (if it occurs at all) under these conditions. Thus the mechanism of interaction

of acetic acid with PVC probably involves either of the two possible molecular processes outlined.

One other feature of the degradation of the blend system deserves discussion and that is the reduction of the amount of material non-condensable at -196°C (see figure (4.3)). However, initiation of non-condensable production occurs at the same temperature in both the mixed and unmixed systems in spite of the fact that acetic acid is being produced at much lower temperatures. This suggests that there is a threshold temperature for this process, and this is compatible with Bamford & Dewar's observations (52) that at lower temperatures, only ketene and water are produced from decomposition of acetic acid, while the decarboxylation reaction, producing methane, and the secondary decomposition of ketene to carbon monoxide and methane, only occur at higher temperatures. The acceleration of deacetylation means that there is less acetic acid available for decomposition at the threshold temperature, and hence less non-condensable material. Also, if ketene is being removed as acetyl chloride by reaction with HCl, this will also contribute to the decrease in the amount of non-condensables.

THERMAL DEGRADATION OF OTHER PVA MIXTURES.

In connection with the work on PVA - PVC mixtures, the degradation of blends of PVA with alloprene, poly(vinylidene chloride) (PVDC), and polychloroprene (PC) was investigated, since each of these polymers produces HCl during degradation.

Alloprene eliminates HCl in high yield during degradation and this is shown in the TVA trace in figure (4.15). Dehydrochlorination commences below 200°C, reaching a maximum at 295°C, and HCl is the sole degradation product of any significance throughout the temperature range shown in the trace. The carbonaceous residue of

this dehydrochlorination undergoes decomposition above 400°C, although this is not shown in figure (4.15).

The dehydrochlorination of PVDC results in discolouration and cross-linking of the polymer (67), one molecule of HCl per monomer unit being evolved.

$$\sim CH_2—CCl_2—CH_2—CCl_2\sim \longrightarrow \sim CH{=}{=}CCl—CH_2—CCl_2\sim \; + \; HCl$$

The proposed mechanism of HCl elimination is free radical in nature (67), although addition of stable free radicals and radical trapping compounds produced anomalous effects. Thus the thermal degradation of PVDC is similar to PVC, although the rate of dehydrochlorination at low temperatures is greater for the former polymer. The TVA trace for PVDC shown in figure (4.16) illustrates these features, HCl being evolved initially below 200°C and reaching a maximum rate at 243°C.

The thermal degradation of PC was studied by Gardner and McNeill (68) who found that the principal stage of dehydrochlorination occurred at higher temperatures than for PVC, under programmed heating conditions; about 90% of the available chlorine being lost as HCl. The TVA trace for PC is shown in figure (4.17) and it can be seen that below 340°C, all the material evolved is non-condensable at -100°C (i.e. HCl), while at 340°C, during dehydrochlorination, evolution of material non-condensable at -196°C commences. Secondary decomposition of the residue of dehydrochlorination occurs mainly above 400°C. The fact that only 90% of the available chlorine in PC is lost as HCl, compared with more than 96% in PVC, was interpreated (68) as a consequence of the fact that in PC degradation the dehydrochlorination and carbonization reactions overlap, whereas in PVC breakdown they are fairly well separated. It was suggested (27) that the mechanism of dehydrochlorination of PC is a non-radical,

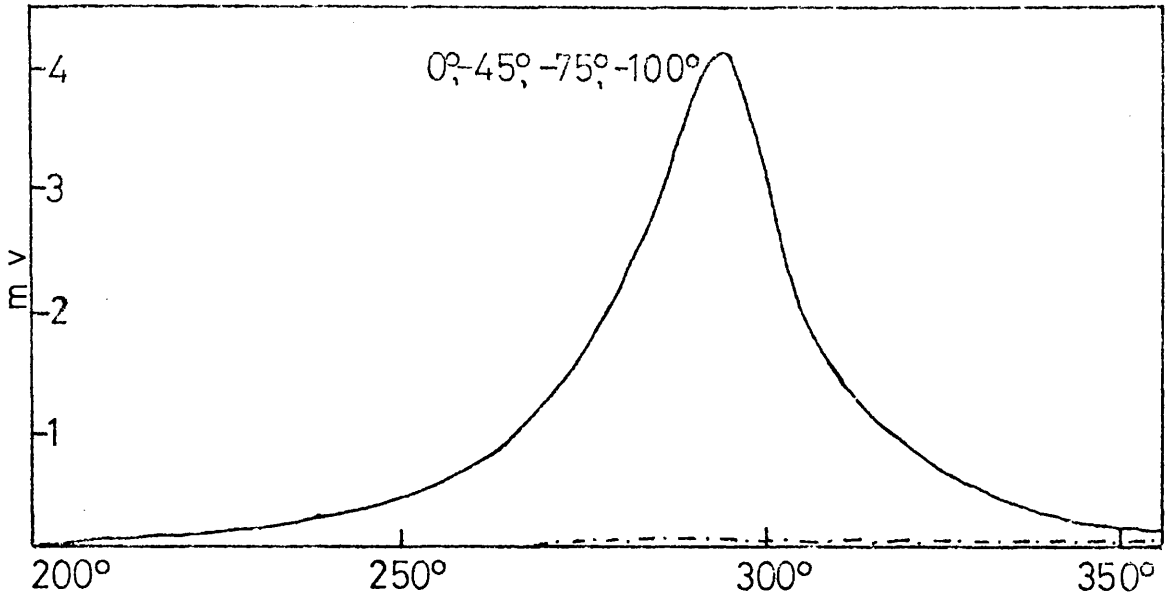


Figure (4.15). TVA trace for 50 mg powder sample of Alloprene. Heating rate 5°C/min.

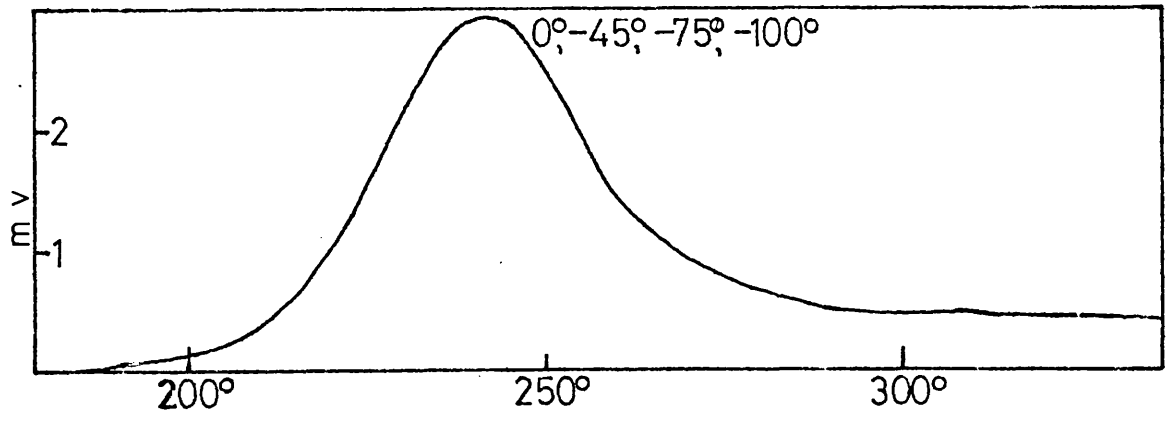


Figure (4.16). TVA trace for 50 mg powder sample of PVDC. Heating rate 5°C/min.

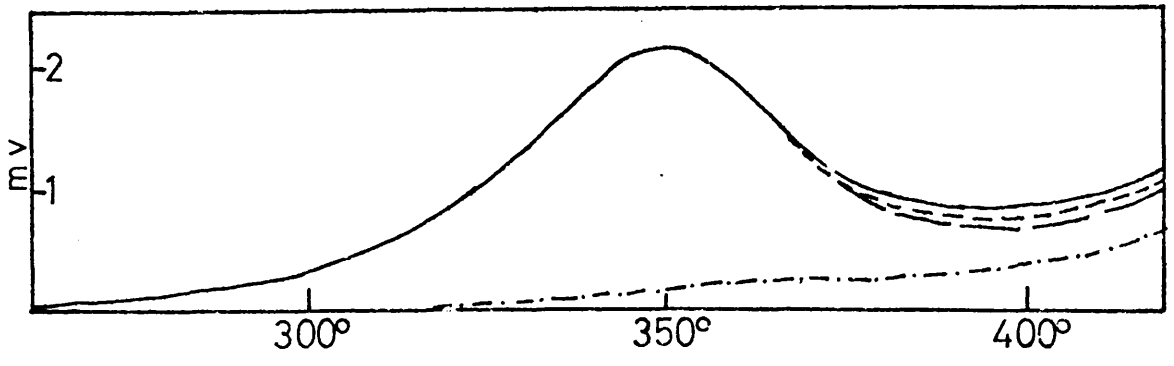
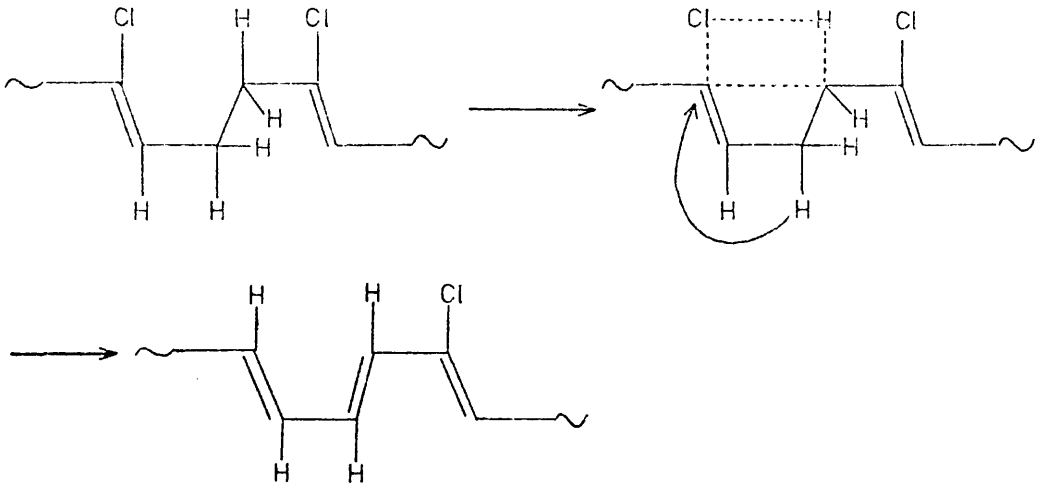


Figure (4.17). TVA trace for 50 mg film sample of PC, cast from benzene. Heating rate 5°C/min.

intra-molecular process shown below :-



ALLOPRENE - PVA BLENDS.

TVA traces for equal weights of PVA (BDH) and alloprene as mixed and unmixed film samples are shown in figure (4.18). For the unmixed case, the TVA peaks for alloprene and PVA overlap, the alloprene volatilization occurring at lower temperatures than that for PVA. The peak at lower temperatures consists mainly of HCl (non-condensable at -100°C), with a small amount of material condensable at -75°C from PVA deacetylation. For the mixed sample, deacetylation is considerably accelerated as shown by the production of acetic acid (condensable at -75°C) at temperatures as low as 200°C. The broad peak above 300°C (for PVA volatilization) in the unmixed system has been reduced to a shoulder, such is the rate of deacetylation at lower temperatures. The rate of production of HCl is relatively unchanged, while the amount of material non-condensable at -196°C is reduced almost to zero in the mixed samples.

All these features are manifested in mixed powder systems too, although to a slightly smaller degree, as shown in figure (4.19). The interaction characteristics are independent of the solvent used to prepare the films, both toluene and methylene chloride being employed in this work. The same qualitative features were also

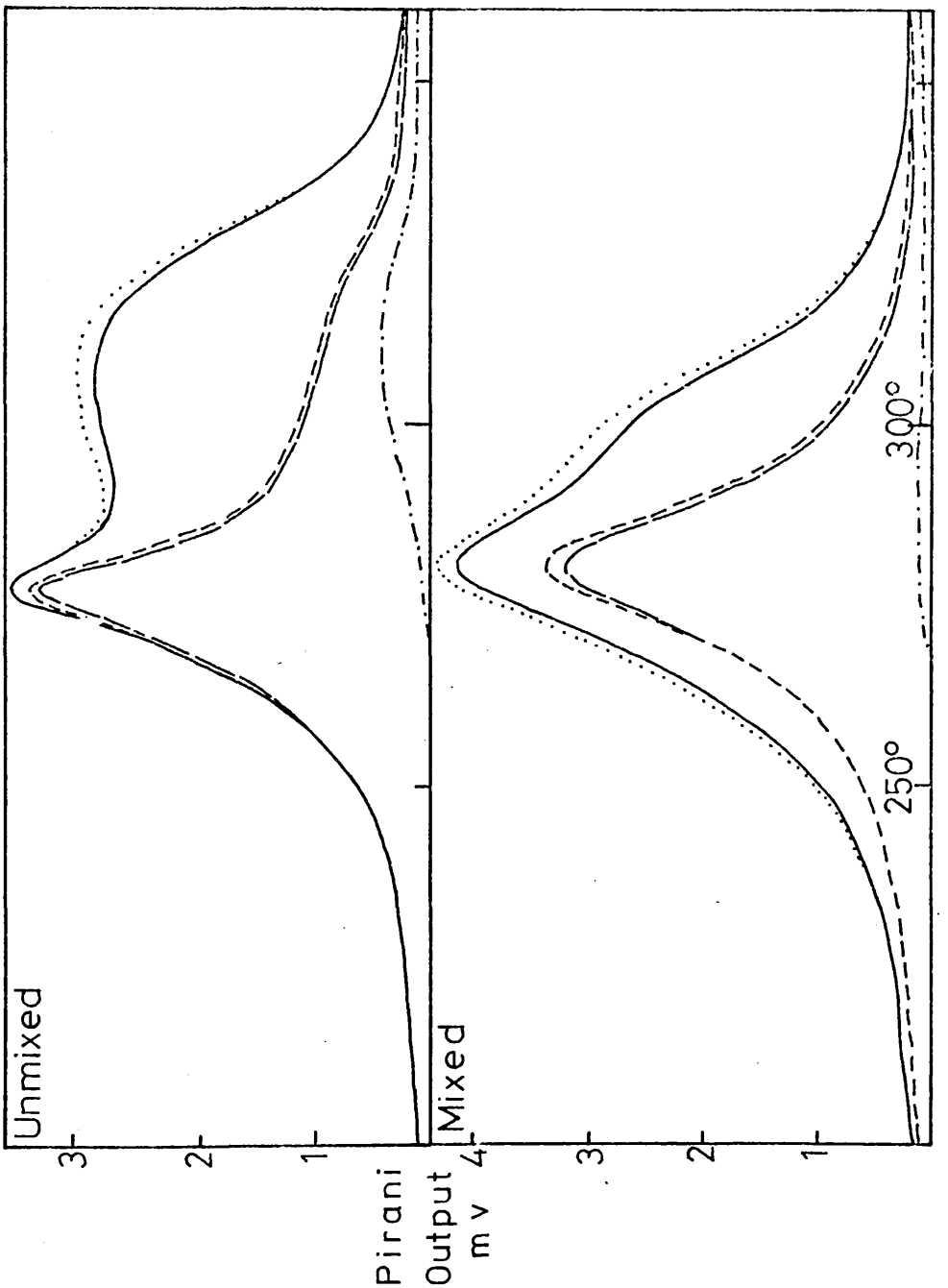


Figure (4.18). TVA curves for equal amounts of PVA (BDH) and Alloprene (30 mg of each polymer), degraded as unmixed and mixed films at 5°C/min. Solvent $MeCl_2$.

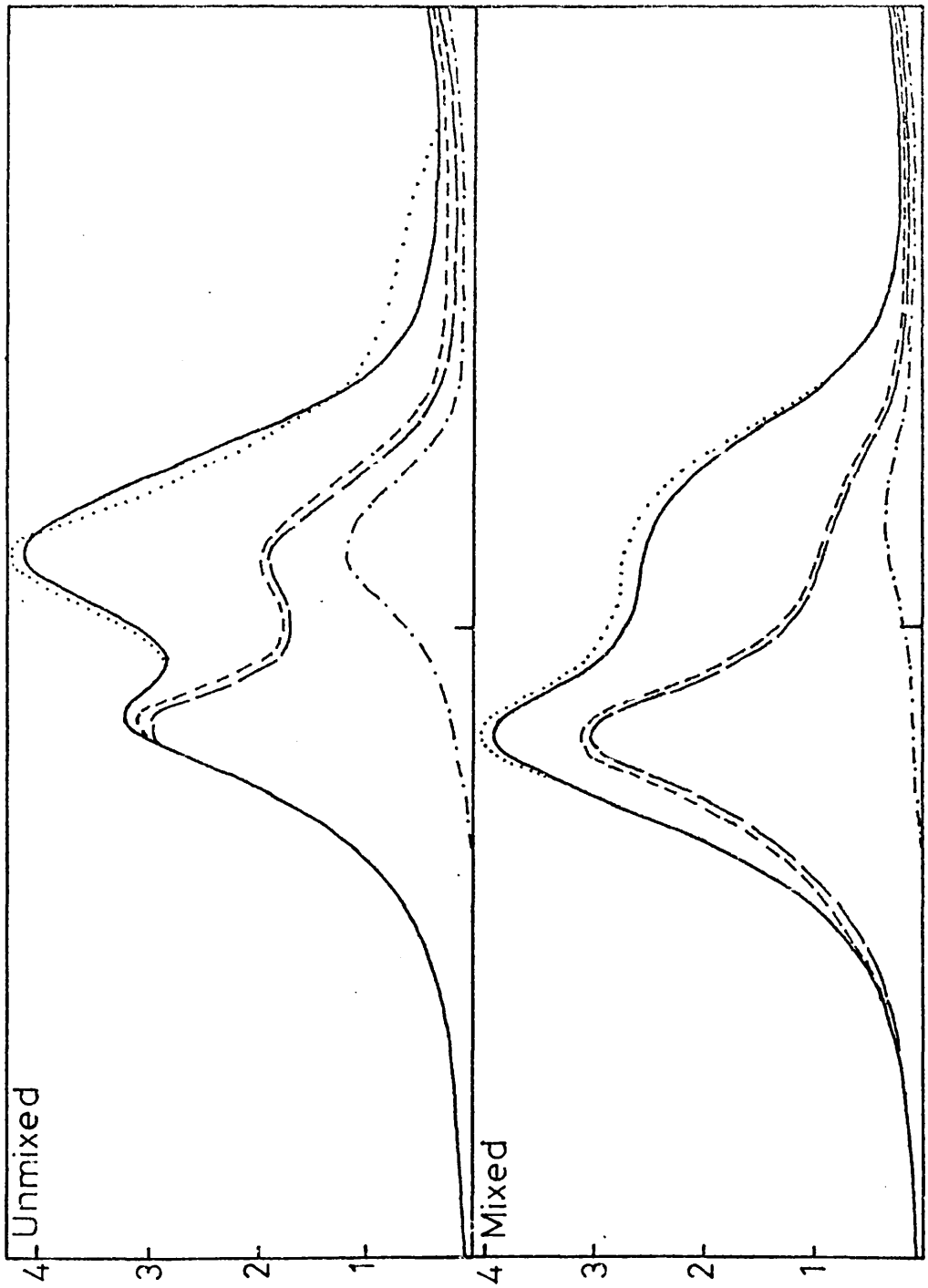


Figure (4.19). TVA curves for equal amounts of PVA (BDH) and Alloprene (30 mg of each polymer), degraded as unmixed and mixed powders at 5^{0}C/min.

observed when the ratio of the polymers was varied, 5:1 and 1:5 mixtures by weight of PVA : PVDC being studied. Analysis of the degradation products by infra-red spectroscopy gave similar results to those from PVA - PVC blends; viz. the absence of ketene and the formation of small amounts of acetyl chloride, besides the products obtained from degradation of the homopolymers.

Thus HCl from degrading alloprene is producing a similar accelerating effect on PVA deacetylation as HCl from degrading PVC, while the effect of acetic acid on degrading alloprene is negligible. Although film samples of PVA and alloprene are not homogeneous, being slightly cloudy in appearance, the contact between the two phases is much more intimate than in the powder system, and hence the interaction is much more pronounced. However, it is impossible to say if this increased interaction is due to the migration of chlorine radicals from the alloprene domains to the PVA domains, causing a radical type interaction with PVA and acceleration of deacetylation, or if the whole accelerated deacetylation issue is a result of a molecular interaction between HCl and PVA as previously described.

POLY(VINYLIDENE CHLORIDE) - PVA BLENDS.

TVA traces for equal amounts of PVA (BDH) and PVDC, degraded simultaneously as mixed and unmixed powder samples are shown in figure (4.20). The unmixed system shows two separate peaks for dehydrochlorination of PVDC and deacetylation of PVA. The mixed system also shows two peaks, but the production of material condensable at -75°C commences around 240°C, indicating an accelerated rate of deacetylation. The production of HCl is relatively unaffected, while the production of material non-condensable at -196°C is considerably reduced. The reduction in height of the PVA peak is probably due to the decrease in the

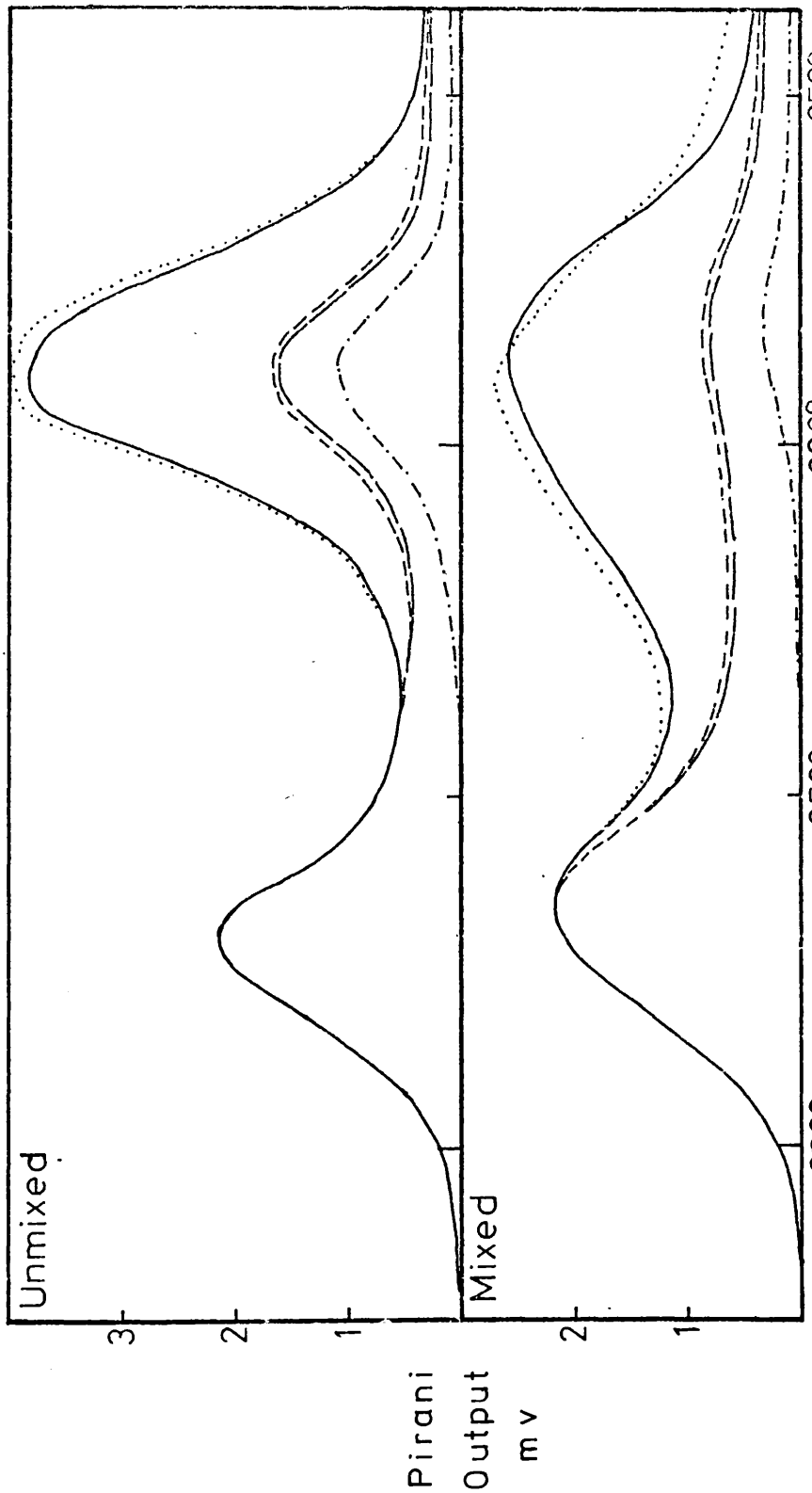


Figure (4.20). TVA curves for equal amounts of PVA (BDH) and PVDC (30 mg of each polymer), degraded as unmixed and mixed powders at 5°C/min.

non-condensables production and also to the fact that acetic acid is being evolved at considerably lower temperatures.

Infra-red analysis of the degradation products gave the same results as for PVA-PVC and PVA-alloprene blends. Thus once more HCl from a degrading polymer is causing acceleration of deacetylation of PVA. Acetic acid appears to have no effect on the dehydrochlorination of PVDC, although this might be expected since HCl does not accelerate PVDC degradation (63).

POLYCHLOROPRENE - PVA BLENDS.

TVA traces for equal amounts of PVA (BDH) and PC degraded simultaneously as mixed and unmixed films are shown in figure (4.21). The unmixed trace shows one peak (for PVA deacetylation) with a shoulder on the high temperature side resulting from dehydrochlorination of PC. The mixed system shows a reduction in the amount of material non-condensable at -196^{o}C and this causes a reduction in the peak height for PVA deacetylation. The rate of production of acetic acid is unaffected as is the rate of dehydrochlorination from PC. These facts have also been observed for 5:1 and 1:5 ratio by weight mixtures of PVA and PC.

Thus this system differs from the previous ones in that HCl from degrading polymer does not accelerate PVA deacetylation. However, under programmed heating conditions the dehydrochlorination of PC occurs at higher temperatures than deacetylation of PVA, and thus it is reasonable that there should be no effect on acetic acid production, which is proceeding rapidly before HCl is evolved from PC. Acetic acid appears to have no effect on the dehydrochlorination of PC, but this is not unreasonable since autocatalysis was not observed during decomposition of PC (68).

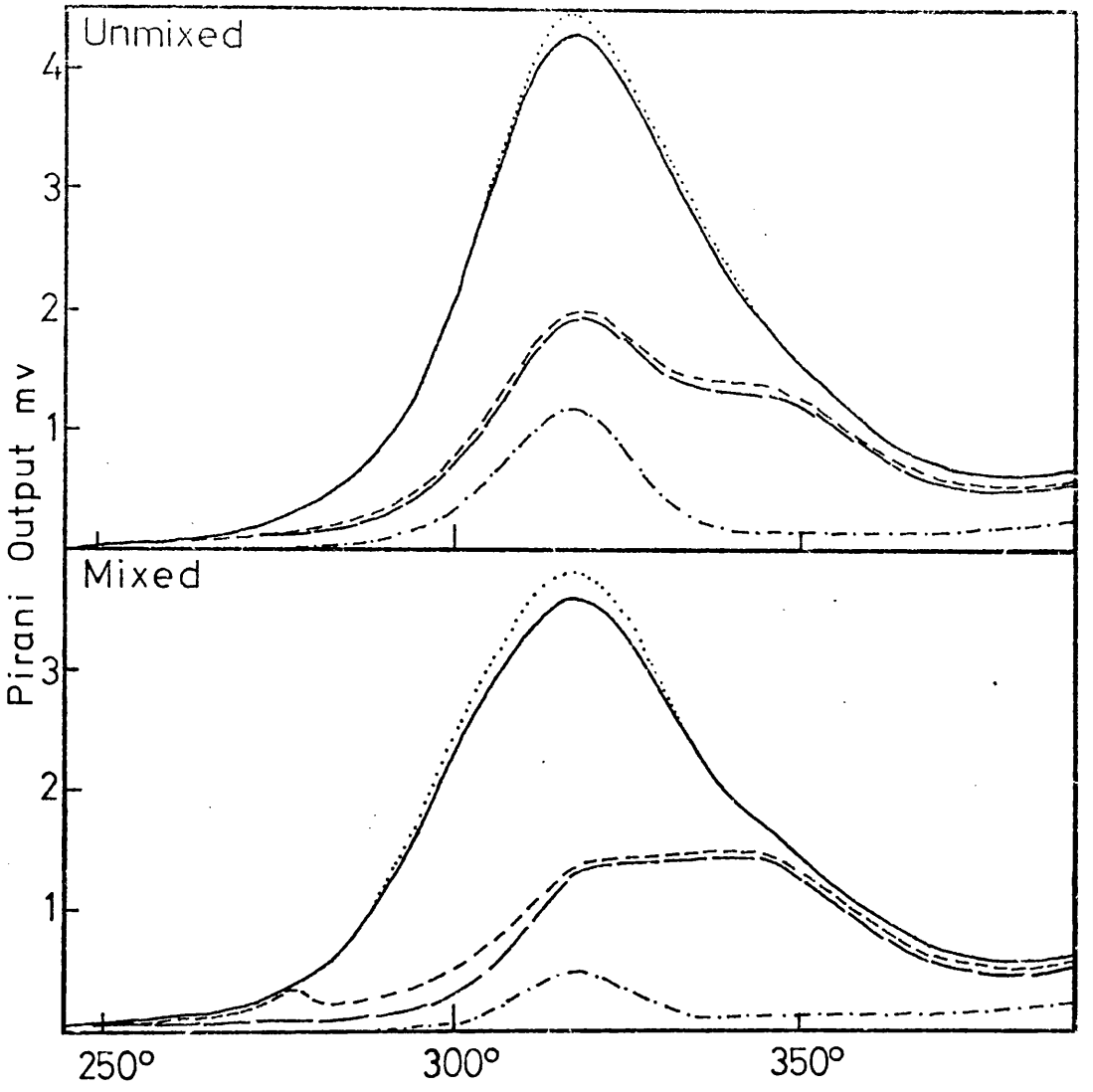


Figure (4.21). TVA curves for equal amounts of PVA(BDH) and PC (30 mg of each polymer), degraded as unmixed and mixed films at 5°C/min. Solvent benzene.

The one interaction which does occur in this system is the reduction of material non-condensable at -196°C in the mixed system, and so it appears reasonable that if ketene decomposes to give carbon monoxide and methane as outlined previously, then the reaction of ketene with HCl to yield acetyl chloride accounts for this reduction.

SUMMARY.

It was observed that HCl from degrading polymers can initiate and accelerate the deacetylation of PVA. This was also observed for degradation of PVA in an atmosphere of HCl. Acetic acid from degrading PVA, has a small accelerating effect on the dehydrochlorination of PVC, but no effect on the degradation of alloprene, PVDC or PC. The removal of ketene by reaction with HCl to form acetyl chloride has the effect of reducing (eliminating in some cases) the amount of material evolved during PVA deacetylation which is non-condensable at -196°C (carbon monoxide and methane).

CHAPTER FIVE

THE THERMAL DEGRADATION OF POLY (VINYL ACETATE) - POLYSTYRENE BLENDS

In view of the interactions occurring during degradation of PVA with PVC and with PMMA, it is of interest to investigate the degradation of other polymer blends containing PVA in an attempt to detect other interactions taking place during degradation. This chapter concerns the degradation of PVA with polystyrene (PS), and to a lesser extent with polyisobutene (PIB), polyethylene (PE) and polypropylene (PP).

INTRODUCTION.

A great deal of research has been done on the degradation of PS, and this has been reviewed by Cameron and MacCallum (69). The volatile products of degradation are monomer in approximately 45% yield, together with progressively decreasing amounts of dimer, trimer, etc; these can be satisfactorily accounted for in terms of the general radical mechanism for depolymerization by depropagation and by intramolecular transfer at chain ends respectively. In addition, an initial rapid decrease in molecular weight is observed and to explain this phenomenon two arguments have been advanced, viz, the scission of a limited number of "weak links" distributed at random in the PS chain, and the intermolecular transfer and/or random scission theory.

The degradation of PE was discussed in chapter one as an example of one extreme form of chain scission reaction involving intra and intermolecular transfer, the low monomer yield ($< 1\%$) illustrating the unimportance of depolymerization. For PP, the effect of the

of the methyl group is to decrease intermolecular transfer and the proportion of products formed by intramolecular transfer increases, so that volatile products are present in greater quantity than for PE, although the yield of monomer is still very small (2). The molecular weight of PP decreases in very much the same way as that of PE in the temperature range 230°-300°C.

For PIB degradation, transfer becomes much less important than for PE and PP, (4), and depolymerization to monomer is a major reaction (32% monomer yield). In fact, there is no other less volatile product present in significant quantity, although low molecular weight chain fragments arise from chain scission (2). Comparing rates of volatilization at corresponding temperatures, PIB is far less stable than PP and PE.

The degradation of PVC-PS blends was studied, using TVA, by McNeill et al (28), who found that both dehydrochlorination and styrene volatilization were retarded. The T max for the latter process was only slightly affected, but the peak shape was considerably altered, with a greater proportion of the degradation of PS occurring at higher temperatures. It was suggested that if chlorine radical attack occurs on the PS, then the PS macroradicals produced are unable to undergo depolymerization at 300°C, although some structural change takes place, leading to increased thermal stability of PS. Cross-linking, or alternatively, chain scission to give molecules with stable end structures were suggested as possibilities for this structural alteration.

POLYMERS USED.

The PVA samples used in this work were those described previously in chapter three. For the most part two PS samples were used; PS-1 (Mn 80,800) was prepared by bulk polymerization at 100°C using

0.09% benzoyl peroxide as initiator; PS-2 (Mn 324,000) was also prepared in bulk, at 60°C, using 0.02% benzoyl peroxide as initiator. Both samples were purified by precipitation in methanol from benzene solution, and dried under vacuum.

The PE sample was a Shell low density commercial polymer, while the PP used was I.C.I. "Propathene" MF 20 purified by precipitation. PIB (Mn 49,100) was prepared (by Dr. R. McGuchan) in methylene chloride at -78°C using stannic chloride as initiator.

RESULTS.

THERMAL VOLATILIZATION ANALYSIS.

TVA traces for PS-1 and PS-2 are shown in figure (5.1). Both traces are very similar with Tmax's of 418° and 424°C respectively. For both samples, the 0° and -45°C traces are coincident, indicating absence of condensation at -45°C, but the -75°C traces show a small limiting rate (for the distillation of a product from the -75°C trap to the liquid nitrogen trap). At -100°C there is complete condensation of products and it has been shown that styrene is condensed at -100°C and has a limiting rate at -75°C, indicating that the TVA peak for PS is due to the volatilization of styrene monomer (34). This is consistent with the known degradation behaviour of PS which gives 40% styrene plus dimer, trimer and higher homologues. With the possible exception of dimer, all products other than monomer would be expected to collect as cold ring fraction. The colourless oil obtained as cold ring fraction, when analysed by infra-red spectroscopy, gives a spectrum almost identical to that for PS, thus confirming expectations that the oil consists of higher homologues of styrene, or alternatively, low molecular weight polymer.

Figure (5.2) shows TVA traces for 1:1 by weight unmixed and mixed film samples of PVA (BDH) and PS-2, degraded at 5°C/min. The

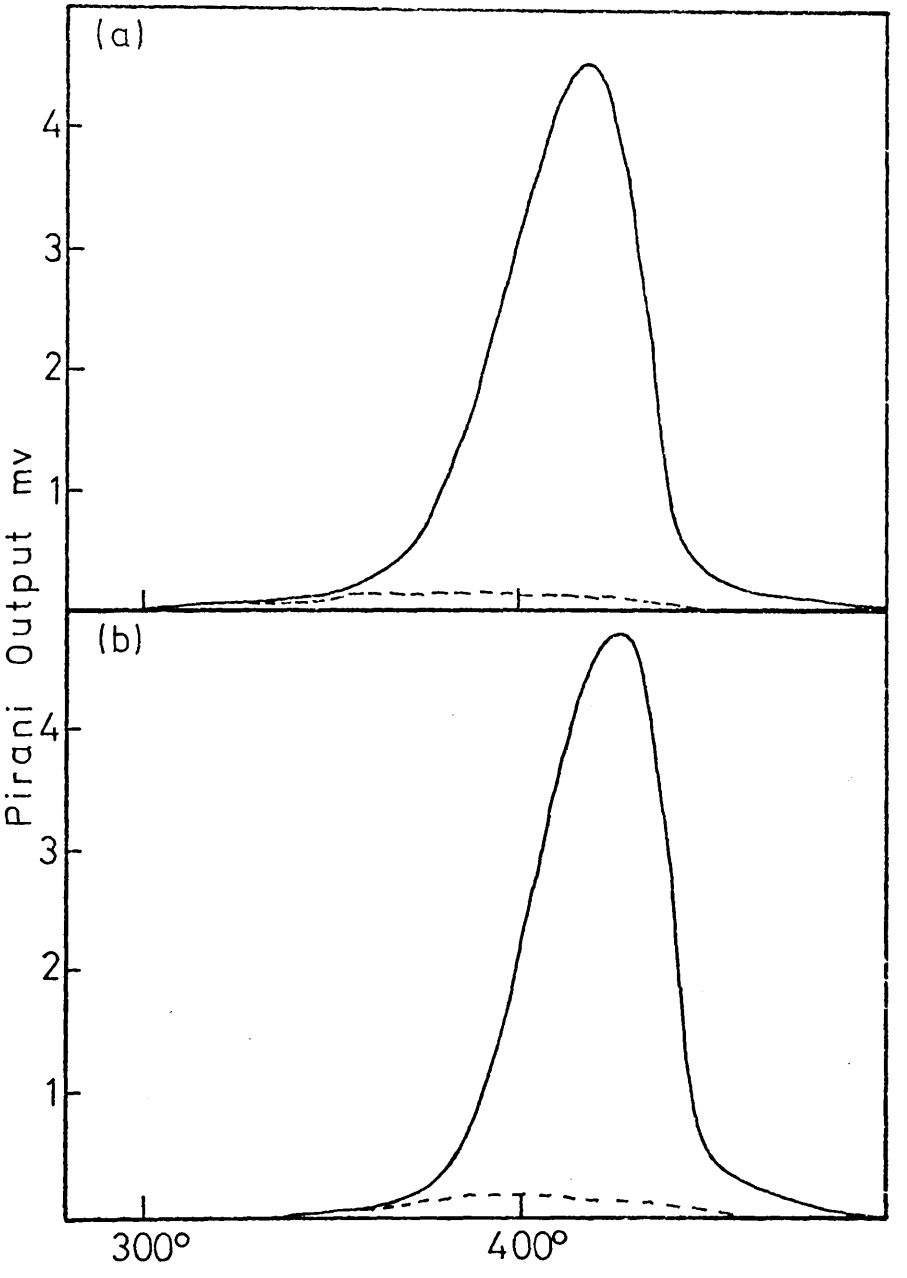


Figure (5.1) TVA curves for (a) PS-1, 50 mg, (b) PS-2, 50 mg; powder samples at a heating rate of 10°C/min. Key for cold trap traces as described on p.35.

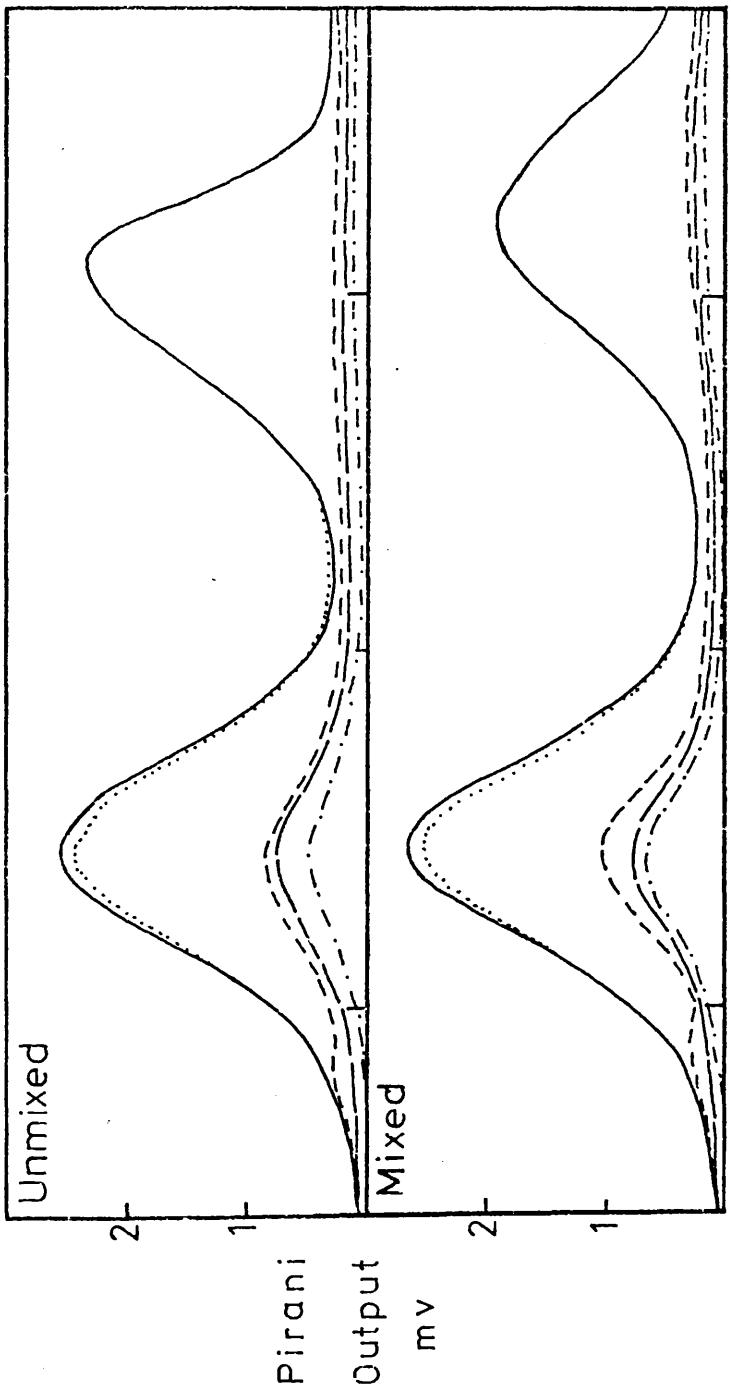


Figure (5.2). TVA traces for equal amounts of PS-2 and PVA (BDH), (20 mg of each polymer), degraded as film samples at 5°C/min. Solvent toluene.

unmixed sample gives two distinct peaks for volatilization from PVA and PS, and that for the latter polymer occurring at higher temperatures. The mixed sample is fundamentally similar, but has some small differences from the unmixed system. In the mixed sample, the Tmax for PVA is shifted slightly to higher temperatures (320^{o} to $324^{o}C$) and the PS peak is broader and has its Tmax at higher temperatures ($429^{o}C$ compared with $408^{o}C$). This small delay in deacetylation and increase in stability of PS, is similar to the effects observed in PVC - PS blends on degradation (28). The nature of condensability of the volatile products is, however, unchanged in the mixed system.

The effect of changing sample form was examined using unmixed powder samples of PVA (BDH) and PS-1 and mixed coprecipitated samples of these polymers. Equal weights of both polymers in chloroform solution were thoroughly mixed as described previously and the mixed solution poured into petroleum ether. The mixed, coprecipitated polymer sample was filtered and dried under vacuum. The TVA results are shown in figure (5.3). The effects noted for the film samples are observed for this system; viz, an increase in Tmax for PVA from 342^{o} to $347^{o}C$, a broadening of the PS peak and increase in its Tmax from 419^{o} to $430^{o}C$. The difference in respective peak heights for PVA and PS between the unmixed and coprecipitated systems (increase in PVA peak height, decrease in PS peak height for the mixed compared to the unmixed system), indicates that the coprecipitation procedure is more effective for PVA than for PS, resulting in a mixed coprecipitated sample which is not exactly 1:1 by weight, but contains an excess of PVA over PS.

It was observed that varying the rate of heating ($5^{o}C$ and $10^{o}C$/min) and the solvent used to prepare films (toluene and chloroform), produced qualitatively the same volatilization behaviour in the TVA apparatus. Also, varying the ratio of weights of the polymers produced

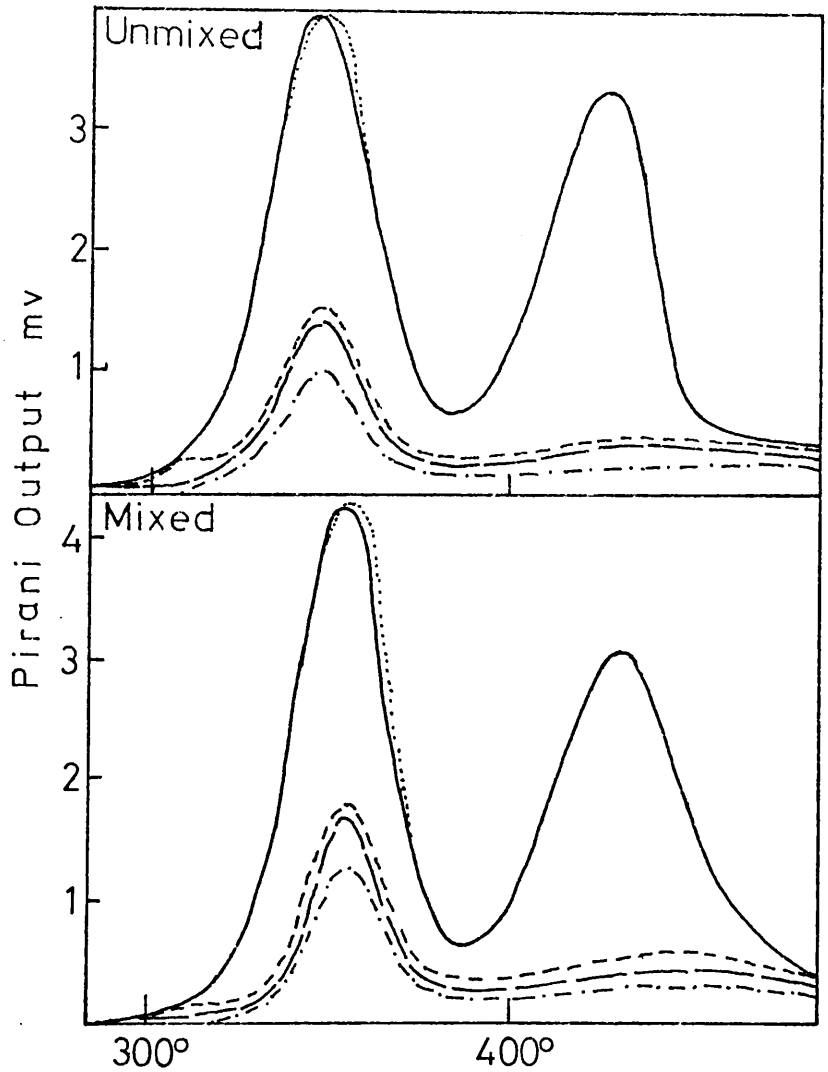


Figure (5.3). TVA traces for PS-1 and PVA (BDH) degraded (a) simultaneously as unmixed powders (20 mg each polymer), (b) simultaneously as a mixed coprecipitated sample (total weight 40 mg) at 10°C/min.

the broadening of the PS peak and increase in its Tmax. Figure (5.4) illustrates the TVA traces for 5:1 by weight of PS-2 : PVA unmixed and mixed films, the Tmax for PS in the mixed film being 412°C, compared to 405°C for the unmixed sample. However, there is little or no effect on the rate of deacetylation in these samples.

VOLATILES ANALYSIS

Analysis by infra-red spectroscopy of the volatile products from degradation to 500°C (at 10°C/min) of a 1:1 by weight mixed film of PVA and PS, revealed only those products obtained from degradation of the homopolymers, viz, styrene and acetic acid in substantial amounts, with ketene and carbon dioxide in small quantities.

Estimations of acetic acid from degradations at 342°C for 1 hour, of film samples of PVA, and PVA mixed with five times its own weight PS-2, were carried out; the acetic acid being collected and titrated against standard sodium hydroxide as before. On average, acetic acid obtained from PVA degraded on its own accounted for 91.7% of the total, theoretically possible deacetylation, while from the mixed sample the corresponding amount was 90.8%. This may indicate a slight delay in the rate of deacetylation, or an actual reduction in the amount of acetic acid produced, from PVA when it is degraded as a mixture with PS. However the effect is quantitatively very small and deductions cannot be drawn with any degree of certainty.

RESIDUE ANALYSIS.

Mixed films of PS - 1 and PVA (5:1 by weight) were degraded at 322°C for 2 hours. The residue was extracted by shaking with toluene for 24 hours and the polymer precipitated in petroleum ether. The polymer was dried under vacuum at 40°C for 24 hours and then examined by infra-red spectroscopy (as KBr discs) and by TVA.

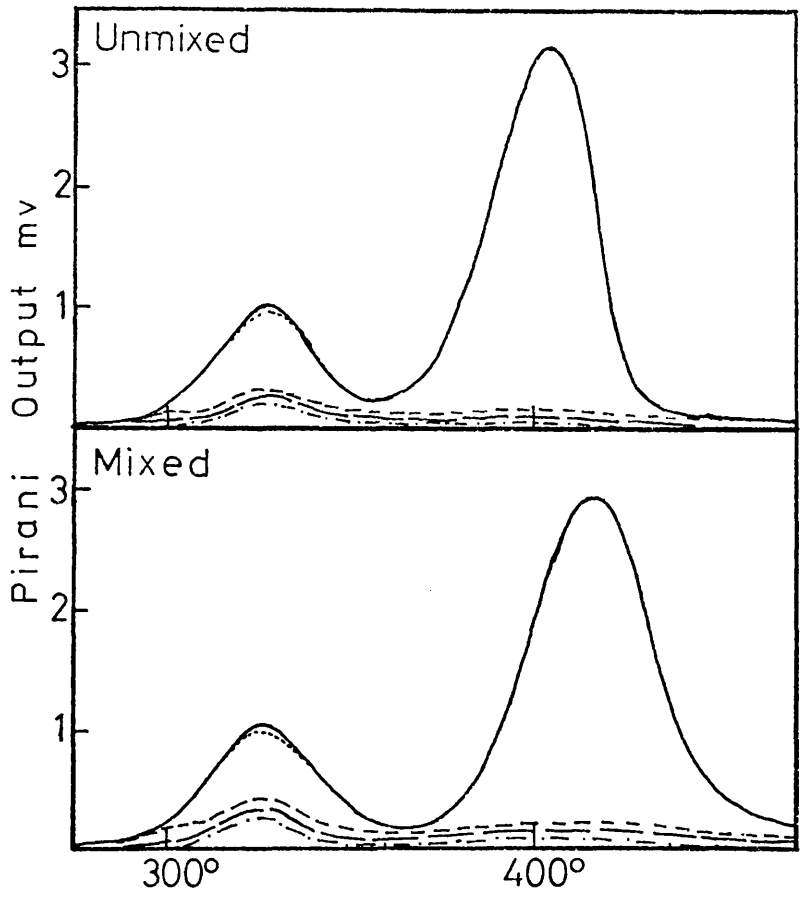


Figure (5.4). TVA traces for PS-2 and PVA (BDH) (5:1 ratio by weight), degraded simultaneously as unmixed and mixed films. Heating rate 10°C/min Solvent toluene.

Figure (5.5) shows the infra-red spectrum of this extracted material and also of the original PS-1 sample, and it may be seen that these spectra are almost identical. The TVA trace for the extracted material was also identical to that for PS-1, the same volatiles pattern and T max (418°C) being observed in both cases.

The same results were obtained for a PS-1 sample which had been degraded at 322°C for 2 hours and extracted as before, thus indicating that the extraction of the partially degraded blend system removed PS only, and that this PS was qualitatively unaffected by degradation in the presence of PVA. It is not surprising that no PVA should be extracted after this thermal treatment at 322°C, since almost complete deacetylation of PVA has occurred leaving the insoluble polyene residue.

MOLECULAR WEIGHT DETERMINATIONS.

100 mg film samples of PS-1 and PS-2 were heated at 322°C for 1 hour and the residue dissolved in toluene. The concentration of the solution and the molecular weight of the degraded polymers were determined as described previously. The same weight of each PS sample was then heated under similar conditions as a mixed film with 20 mg of PVA (BDH). The residue, which was brown in colour (deacetylation being almost complete), was extracted with toluene, its concentration estimated and the molecular weight of the partially degraded PS determined as before.

The results of this investigation are presented in Table (5.1) It may be seen that there is a rapid decrease in molecular weight for PS-2 heated in the presence of PVA, while for PS-1 the decrease in molecular weight is smaller than for the sample degraded alone. For the PVC-PS system, although no molecular data was presented, it was suggested (28), that chain scission or cross-linking may be

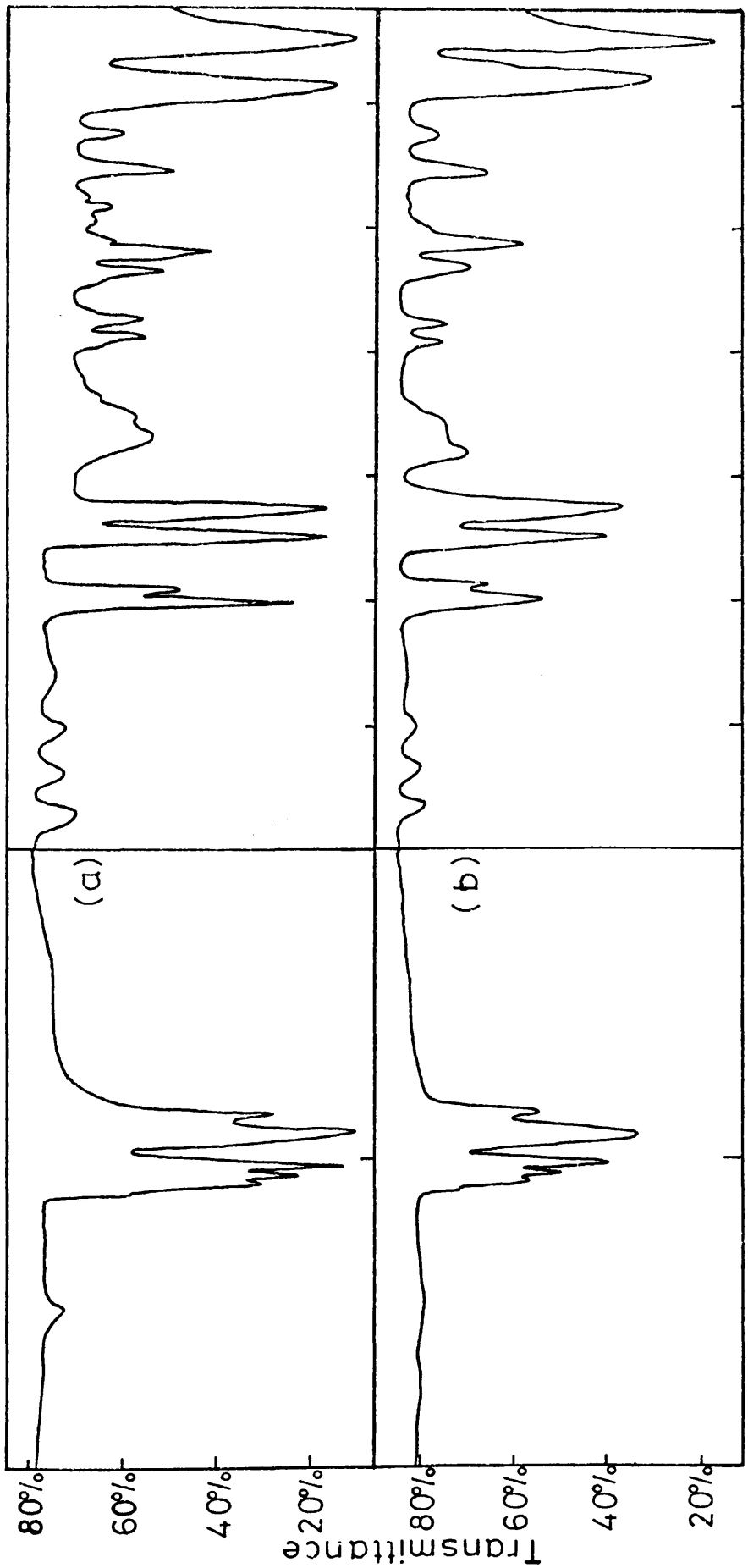


Figure (5.5). Infra-red spectra of (a) PS-1, (b) PS-1 degraded at 322°C for 2 hours with one fifth its weight of PVA (BDH). Samples as KBr discs.

TABLE (5.1)

The effect on the molecular weight of PS-1 and PS-2, for samples heated at 322°C for 1 hour, alone, and as a mixed film with PVA (BDH). Original molecular weights; PS-1, 80,800; PS-2, 324,000.

Sample	Expt.	Mn after heating alone	Mn after heating with PVA
PS-1	1	35,200	49,600
	2	37,900	46,800
PS-2	1	298,000	141,000
	2	308,000	142,000

induced (by chlorine radicals). For the higher molecular weight PS sample in this investigation, it appears that chain scission is occurring during degradation for the mixture with PVA. On the other hand, the effect on the lower molecular weight PS sample cannot readily be explained in terms of increased chain scission, and cross-linking also appears an unlikely explanation.

Both PS samples extracted from the mixed systems were subjected to examination by TVA and infra-red spectroscopy. The extracted samples were identical (apart from molecular weight) to the original PS samples, and hence it would appear that these molecular weight changes cannot account for the increased thermal stability of PS degraded as a blend with PVA.

EFFECT OF THE RESIDUE FROM PVA DEGRADATION ON THE DECOMPOSITION OF PS.

Since the increased thermal stability of PS when it is degraded as a blend with PVA cannot be accounted for by purely structural changes within the PS itself, it is possible that this phenomenon arises from interaction of the degrading PS with the carbonaceous residue of PVA deacetylation. To investigate this possible explanation, TVA studies on the effect of the PVA residue on degrading PS were carried out.

In figure (5.6) the TVA trace (0°C curve only) for PS-2 as a

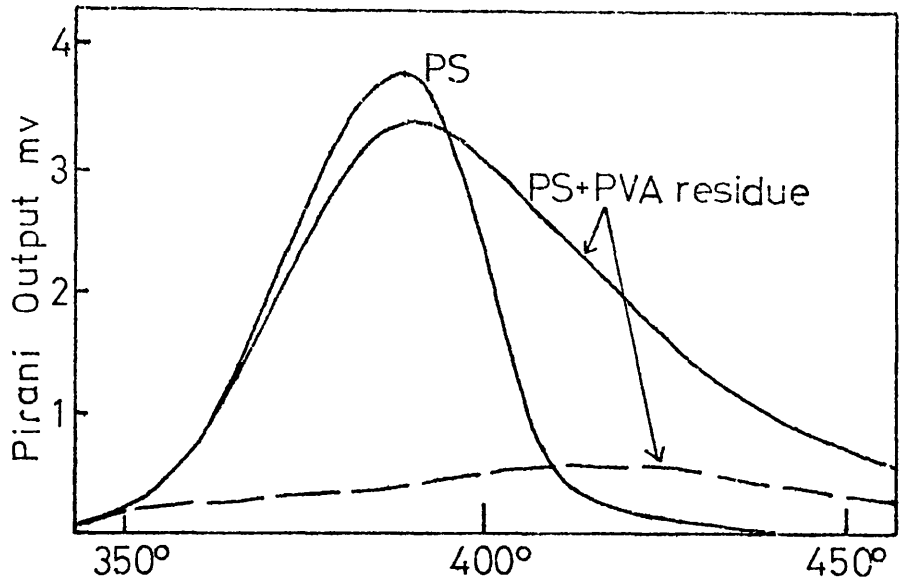


Figure (5.6). TVA traces for (a) PS-2 (50 mg film), (b) PS-2 (50 mg film) mixed with the residue from deacetylation of PVA (BDH). Heating rate 5°C/min; solvent toluene.

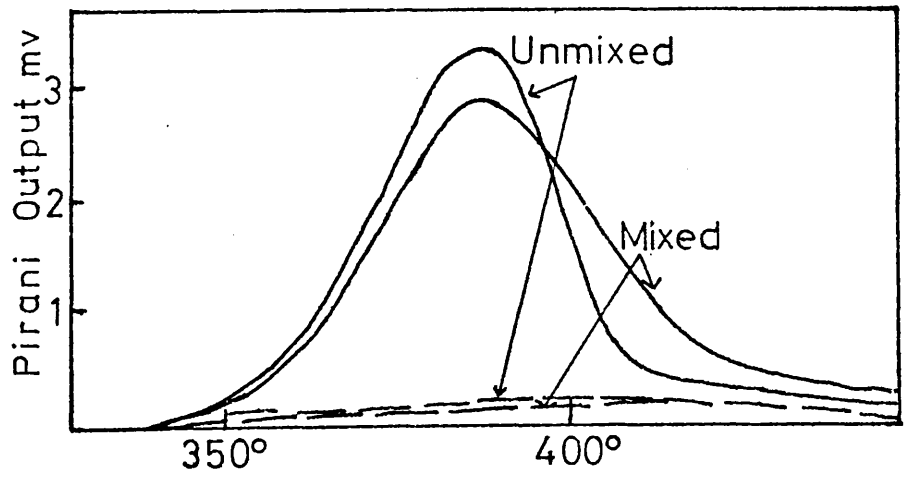


Figure (5.7). TVA traces for PS-2 + the residue of PVA(BDH) degraded simultaneously as unmixed and mixed systems. Sample sizes, 30 mg PS-2, 30 mg PVA (BDH). Heating rate 5°C/min; solvent toluene.

50 mg film degraded at $5^{o}C$/min is presented with the 0^{o} and $-100^{o}C$ traces for an equal amount of PS-2 degraded as a film with the residue of PVA deacetylation. This latter TVA trace was obtained by degrading a 50 mg film of PVA at $5^{o}C$/min until deacetylation was complete; the TVA tube was allowed to cool and then 50 mg of PS-2 in toluene solution was added and the solvent removed under vacuum to give a film of PS-2 and PVA residue, which was degraded to give the trace shown in the figure.

For the PS-2 sample degraded alone, there is no material produced which is non-condensable at $-100^{o}C$, and the peak is similar to that described previously. The mixed sample shows the production of material non-condensable at $-100^{o}C$ from break-up of the conjugated polyene chains of the PVA residue. The $0^{o}C$ trace is smaller, broader and retarded compared to that for the PS sample degraded on its own, although the Tmax is only slightly greater ($393^{o}C$ compared to $391^{o}C$). This delay in styrene volatilization is even more pronounced than is indicated by the behaviour of the $0^{o}C$ traces, since it should be remembered that the volatilization from the PVA residue in the mixed sample also makes a contribution to the magnitude of the $0^{o}C$ trace.

TVA traces of PS-2 and the PVA residue as unmixed and mixed samples are reproduced in figure (5.7) for the 0^{o} and $-100^{o}C$ traces. For the unmixed sample, a 30 mg film of PVA cast in one limb of a twin-limbed TVA degradation tube was degraded at $5^{o}C$/min until deacetylation was complete. The tube was cooled, a 30 mg film of PS-2 cast in the other limb, and the samples in an unmixed state degraded to obtain the "unmixed" trace. For the mixed system, 15 mg film samples of PVA were cast in each limb of the tube and degraded to the same temperature as for the unmixed system, until deacetylation was

complete. The tube was cooled and 15 mg films of PS-2 cast in both limbs and the samples degraded in a mixed state to obtain the "mixed" trace.

The volatilization behaviour of the PVA residue, as depicted by the -100°C traces is similar for both systems, while the styrene volatilization, as shown by the 0°C trace (although this "contains" the PVA residue volatilization) is retarded significantly in the mixed system.

While the physical state of this system (PS films were cast directly on to the smooth brown film residue of PVA), is not the same as that prevailing in the mixed polymer system, it appears that the PVA residue is having a significant delaying effect on the volatilization of styrene. The mechanism of this delaying effect is difficult to elucidate. It could be some type of diffusion or other physical effect, or it may be chemical in nature. Combination of PS macroradicals with PVA polyene radicals could lead to a delay in styrene production, or grafting of PS macroradicals on to the polyene chains as in grafting of vinyl polymers on to polypropylene (24), could be responsible by "removing" a radical centre on the PS chain.

THE DEGRADATION OF BLENDS OF PVA WITH PE, PP AND PIB.

TVA traces for PE, PP and PIB are shown in figure (5.8). For PE, extensive intermolecular transfer results in short chain fragments which condense on the cooled upper part of the degradation tube as cold ring fraction. Even with the 100 mg sample used, the amount of volatile material obtained is small. The lack of coincidence in the four TVA traces indicates a mixture of condensable and non-condensable products, a different amount of material being condensed out at each of the initial cold traps below 0°C.

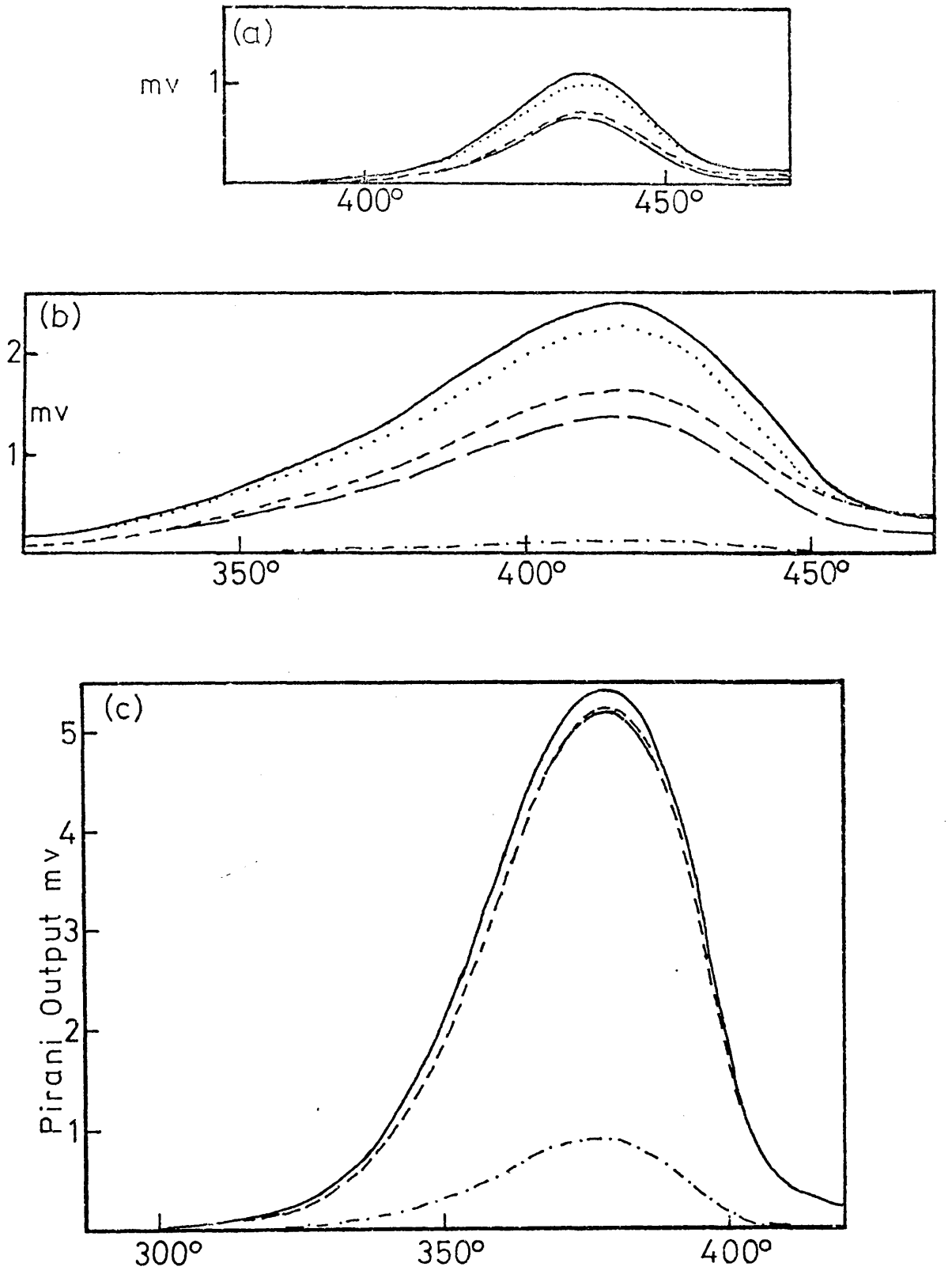


Figure (5.8). TVA traces for (a) PE, 100 mg powder, (b) PP, 100 mg powder, (c) PIB, 50 mg film (from benzene). Heating rate 5°C/min.

For PP, intermolecular transfer is reduced and proportion of products formed by intramolecular transfer increases, so that volatile products are present in greater quantity than for an equivalent amount of PE. The TVA trace indicates the increased amount of volatile material, and shows that a greater fraction of such material than for PE is condensable at -75°C and -100°C. It may also be observed that volatilization from PP commences at lower temperatures than from PE.

For PIB, transfer becomes much less important and depolymerization is the major reaction. From the TVA trace, the major component is material non-condensable at -100°C, which is consistent with the behaviour of iso-butene in the TVA apparatus (34). As can be observed from the TVA trace, iso-butene is not the only volatile product, a small amount of material condensable at -75°C and -100°C, and material non-condensable at -196°C also being evolved. The latter is probably due to methane which is evolved in small quantities during degradation of PIB (2), besides similar amounts of higher hydrocarbons like isobutane, pentenes and neo-pentane which are also products of degradation.

PVA - PE BLENDS.

To obtain a significantly large volatilization peak for PE, it was necessary to use 100 mg samples. 20 mg samples of PVA were used since 100 mg samples gave such large volatilization peaks that the PE behaviour was obscured. Figure (5.9) presents TVA traces for unmixed and mixed 5:1 by weight powder samples of PE and PVA respectively. In both systems, two distinct peaks for PVA and PE volatilization are obtained, and it may be observed that there is little or no difference between the TVA traces for the unmixed and mixed samples. Although it is possible that some form of interaction may be taking place

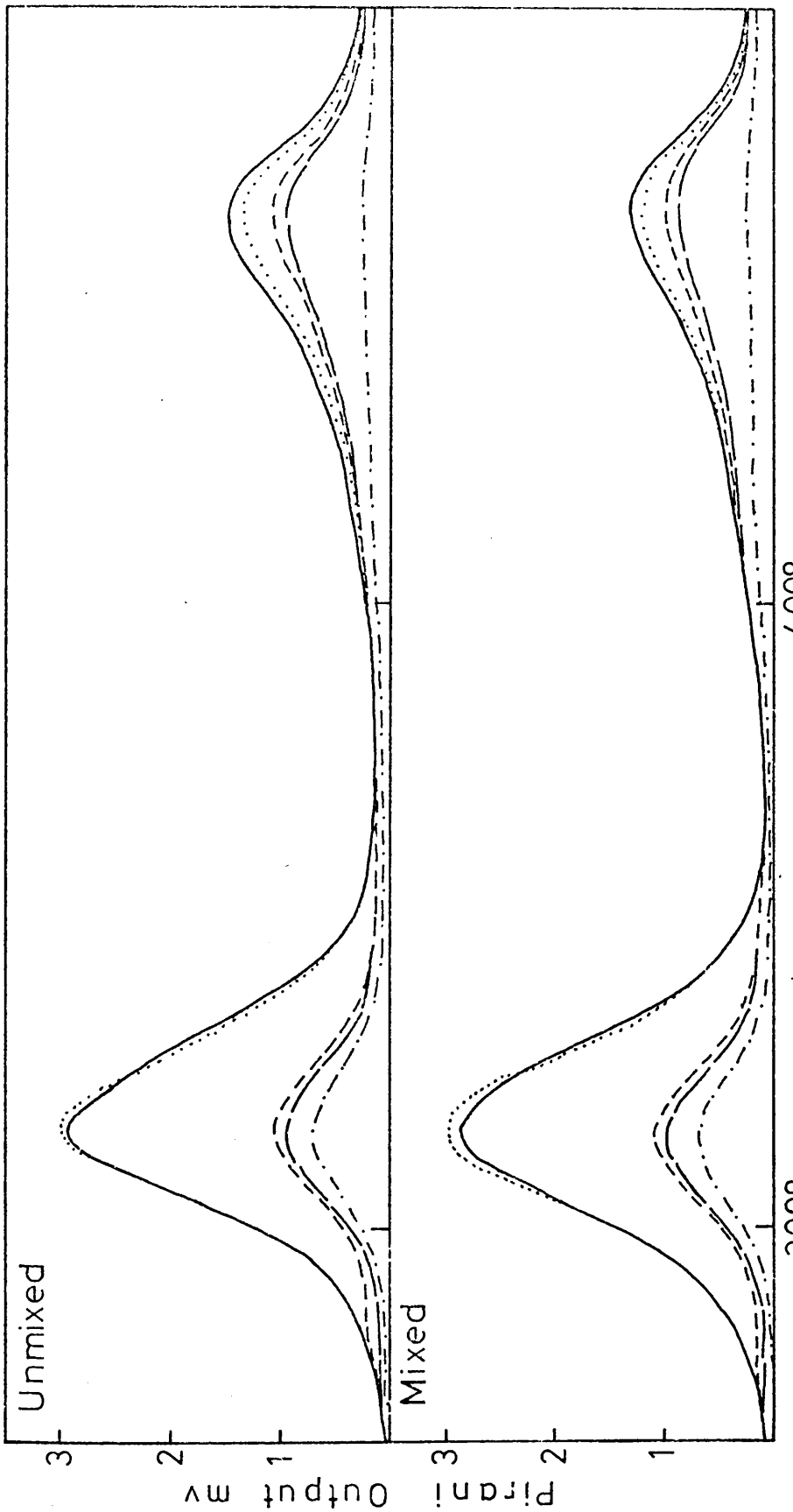


Figure (5.9). TVA traces of PE and PVA (BDH), (5:1 ratio by weight) degraded simultaneously as unmixed and mixed samples (powders). Heating rate 5°C/min. Total sample weight 120 mg.

between the polymers during degradation (e.g. the formation of graft copolymers), there is no detectable effect on the volatilization behaviour of either polymer.

PVA - PP BLENDS.

Similar results to those obtained for PVA - PE blends were obtained from this system. In figure (5.10) the TVA traces for 5:1 by weight unmixed and mixed powder samples of PP and PVA respectively are reproduced, and for both traces, the two peaks corresponding to deacetylation of PVA and volatilization of products from degradation of PP are clearly distinguishable. However, there is little or no difference in volatilization behaviour between the unmixed and mixed samples. Pavlinec and Kaloforov (25) found grafting during the initial stages of the degradation of PVA and PP mixtures, and suggested some form of interaction of radicals from PVA and PP. In view of this it may be surprising that the volatilization behaviour of the blends is not affected.

PVA - PIB BLENDS.

Since the major reaction in PIB decomposition is depolymerization to monomer, it might be expected, in view of the behaviour of PVA-PMMA blends, that degradation of PIB in the presence of PVA would lead to interactions which might be reflected in the volatilization behaviour As may be seen from figure (5.11) for 1:1 by weight unmixed and mixed film samples of PVA and PIB, this is not found to occur, both traces exhibiting two overlapping peaks (the PIB peak occurs at higher temperatures), and an overall volatilization pattern which is almost identical for both systems.

Also, examination by TVA and infra-red spectroscopy of PIB extracted from degradation at 270^{o}C for two hours with an equal amount of PVA, gave identical results to those obtained from PIB

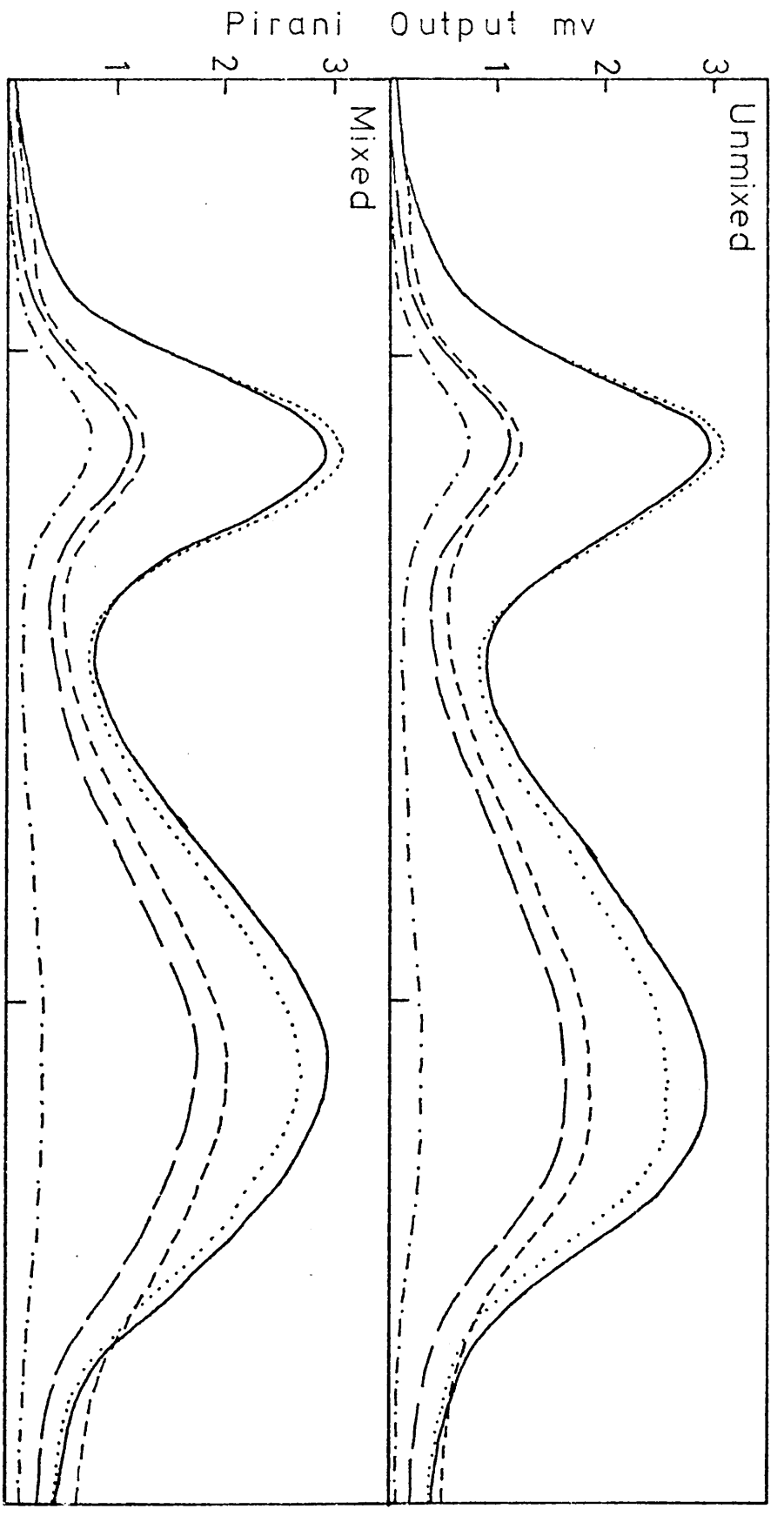


Figure (5.10). TVA traces of PP and PVA (BDH), (5:1 ratio by weight), degraded simultaneously as unmixed and mixed samples (powders). Heating rate 5°C/min. Total sample weight 120 mg.

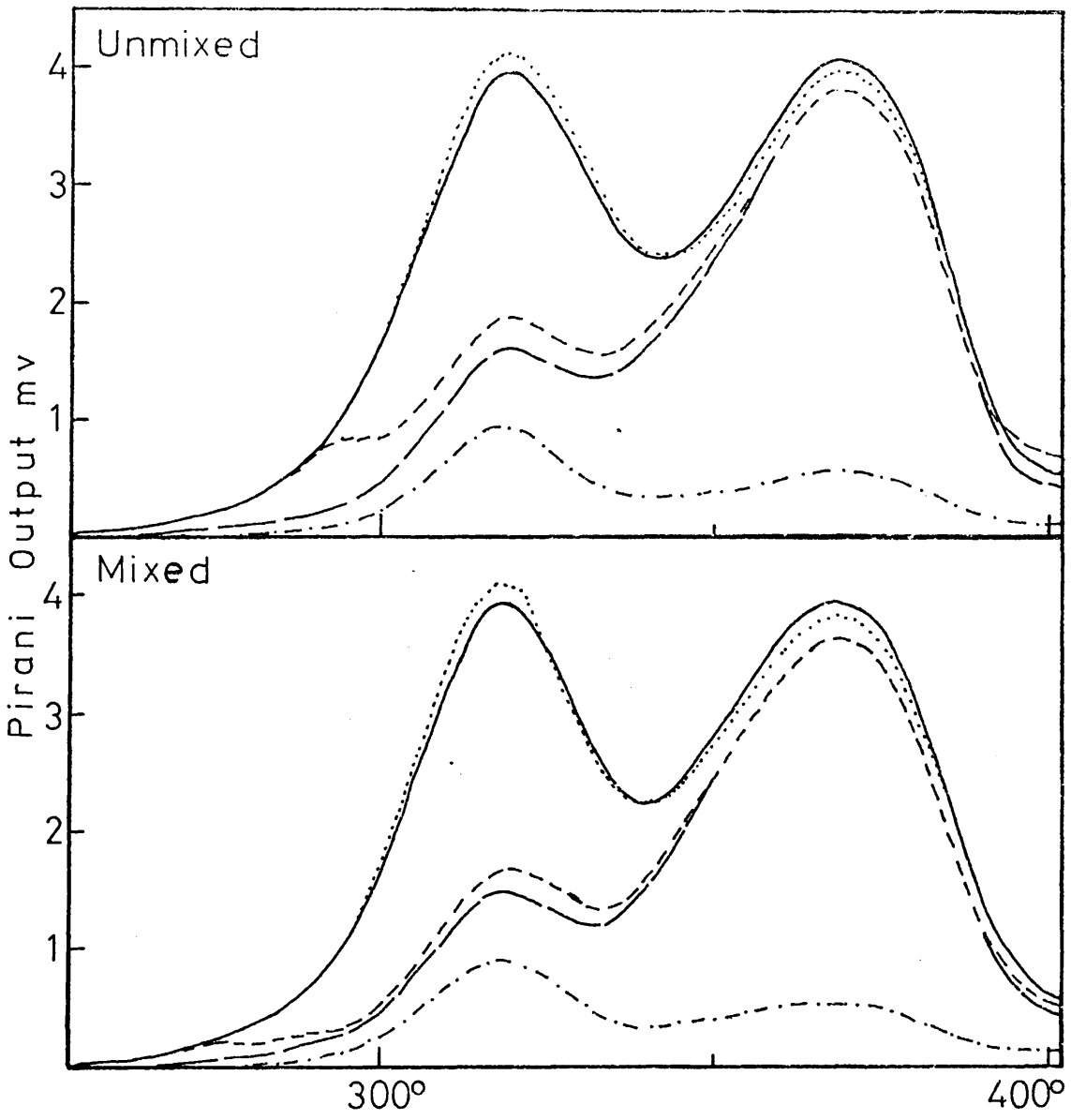


Figure (5.11). TVA traces of PVA (BDH) and PIB (50 mg of each polymer), degraded simultaneously as unmixed and mixed films. Heating 5°C/min.

which had been degraded alone under similar conditions. Both of these PIB samples gave TVA traces and infra-red spectra identical to those for the original PIB sample. Thus besides no difference in the volatilization behaviour of the mixture, there is no qualitative change in the PIB molecules and no grafting of PVA on to PIB, during degradation.

CONCLUSIONS.

During degradation of blends of PVA with PE, PP and PIB, no differences have been observed in the volatilization behaviour of the mixed systems compared with the unmixed systems. In mixtures of PVA with PS, the deacetylation of PVA is only slightly retarded, while there is delay in the rate of production of styrene from PS decomposition. The latter effect is not due to any change in the PS structure, but may involve interaction of PS macroradicals with the carbonaceous residue of PVA deacetylation.

CHAPTER SIX

THE THERMAL DEGRADATION OF SOME VINYL ACETATE COPOLYMERS.

The degradation of PVA when mixed with other polymers has been considered in the preceding three chapters. In this chapter, in an effort to collect information about the effect of the environment on the decomposition of vinyl acetate (VA) units, the thermal behaviour of copolymers of VA with methyl methacrylate (MMA), acrylonitrile (AN), styrene (S) and ethylene (E) has been studied.

INTRODUCTION.

The degradation of VA - MMA copolymers has only briefly been investigated by Daniel and Michel (70) and Gardner (71), who observed production of acetic acid from deacetylation of VA units, and MMA monomer from depolymerization of MMA units. In VA-AN copolymers, it was observed (72) that elimination of acetic acid was concurrent with the degradation reactions occurring in the AN sequences.

Mohammed (73), in a short study of VA-S and VA-E copolymers, suggested that initial degradation takes place favourably at VA sites, which he supposed were the "weak links" in the copolymers. For VA-E copolymers, Gardner (71) noted that two separate reactions were occurring at temperatures independent of the copolymer composition, while Gardner and McNeill (36) observed for the copolymer residues that UV absorption beyond the triene region was almost completely absent.

POLYMERS USED.

Table (6.1) lists the polymers used in this work and also gives brief details of their history; number-average molecular weights are quoted where available and the percentages refer to the mole %

VA content of the copolymer. The VA - MMA copolymers were prepared by Mr. D. Tosh, the VA - S copolymers by Mr. J. McLune; and the VA - AN copolymers by Mr. D. McDonald by a method similar to that of Sorenson and Campbell (74). Unfavourable reactivity ratios (75) made it difficult to produce copolymers with a VA content above 20% in the case of the S copolymers and 40% in the case of the MMA copolymers.

VA - MMA COPOLYMERS.

THERMAL VOLATILIZATION ANALYSIS

TVA traces for the five VA - MMA copolymers are shown in figures (6.1) to (6.5). All the copolymers exhibit only one peak for volatilization although the 5% and 10% copolymers have a small shoulder below 300°C, corresponding to chain end initiated depolymerization of MMA units. As the VA content of the copolymers increases this shoulder disappears. This is caused, not only by depolymerization being unable to pass through the VA groups, but by the extreme unreactivity of the VA group to polymerization, which makes it more probable that the chain ends will consist of VA units.

MMA monomer, however, is evolved throughout the degradation, as can be observed from the limiting rate behaviour of the -75°C trace. As the VA content of the copolymers increases, the amount of material non-condensable at -75°C increases. The temperature of the maximum rate of volatilization for the two homopolymers and the copolymers is shown in Table (5.2). The Tmax increases from PMMA to the 5% and 10% VA-MMA copolymers and then decreases with increasing VA content to the 40% copolymer which has a Tmax slightly lower than PVA itself. The initial increase in Tmax can be explained by the disappearance of chain end initiated depolymerization of MMA units; the subsequent decrease in Tmax towards that for PVA resulting from the increasing VA content, and hence increasing rate of deacetylation,

TABLE 1. POLYMER SAMPLES

Polymer	M_n	History
PVA (BDH)	37,100	B.D.H. Ltd., purified by precipitation.
PMMA	575,000	Bulk polym. at 60°C with 0.05% AIBN(1).
PS - 2	80,800	" " " " " 0.02% Benzoyl Peroxide.
PE	-	I.C.I.'Alkathene', purified by precipitation.
PAN	-	Slurry polym. at 40°C with 0.3g PB/0.15g SB(2)
2% VA-AN	-	" " " " " " " "
5% VA-AN	-	" " " " " " " "
18% VA-AN	-	" " " " " " " "
26% VA-AN	-	" " " " " " " "
41% VA-AN	-	" " " " " " " "
5% VA-MMA	305,000	Bulk polym. at 60°C with 0.1% AIBN
10% VA-MMA	192,000	" " " " " " "
20% VA-MMA	114,000	" " " " " " "
30% VA-MMA	100,000	" " " " " " "
40% VA-MMA	98,000	" " " " " " "
5% VA-S	35,200	" " " " " 0.5% "
10% VA-S	22,100	" " " " " " "
15% VA-S	15,300	" " " " " 0.2% "
20% VA-S	11,000	" " " " " " "
12% VA-E	52,500	I.C.I.'Alathon' 3130, purified by reprecipitation
18% VA-E	43,000	" " 3170, " " "
33% VA-E	22,000	" " 3185, " " "

(1) Azobisisobutyronitrile

(2) Potassium persulphate - sodium bisulphite initiator.

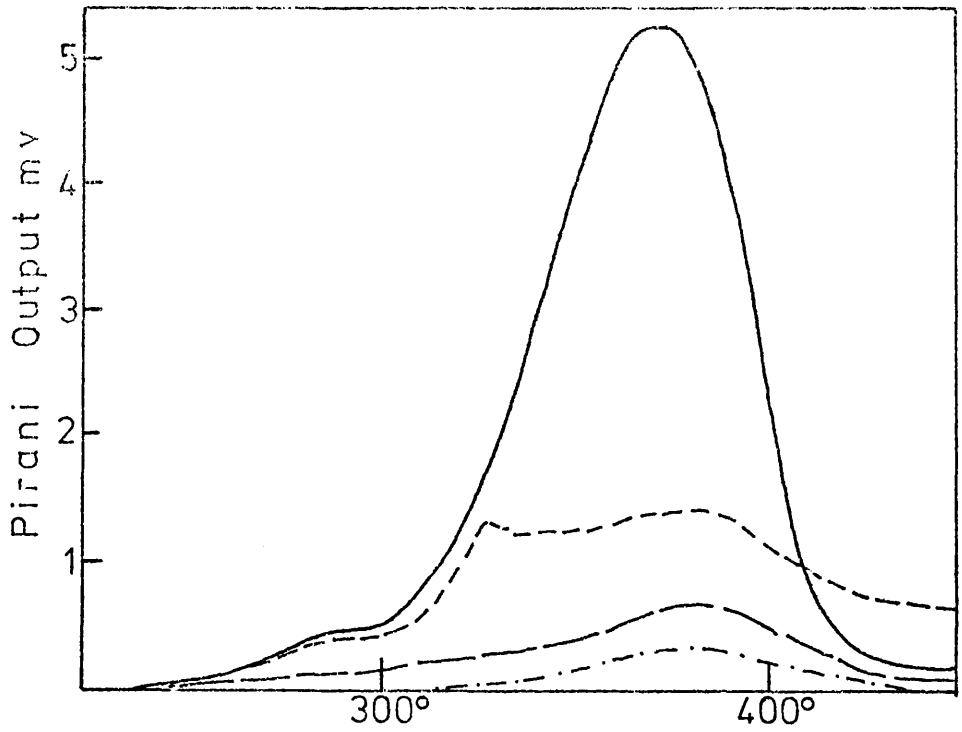


Figure (6.1). TVA curve for the 5% VA-MMA copolymer. Heating rate 10°C/min, 50 mg powder sample. Key to traces as on p.35

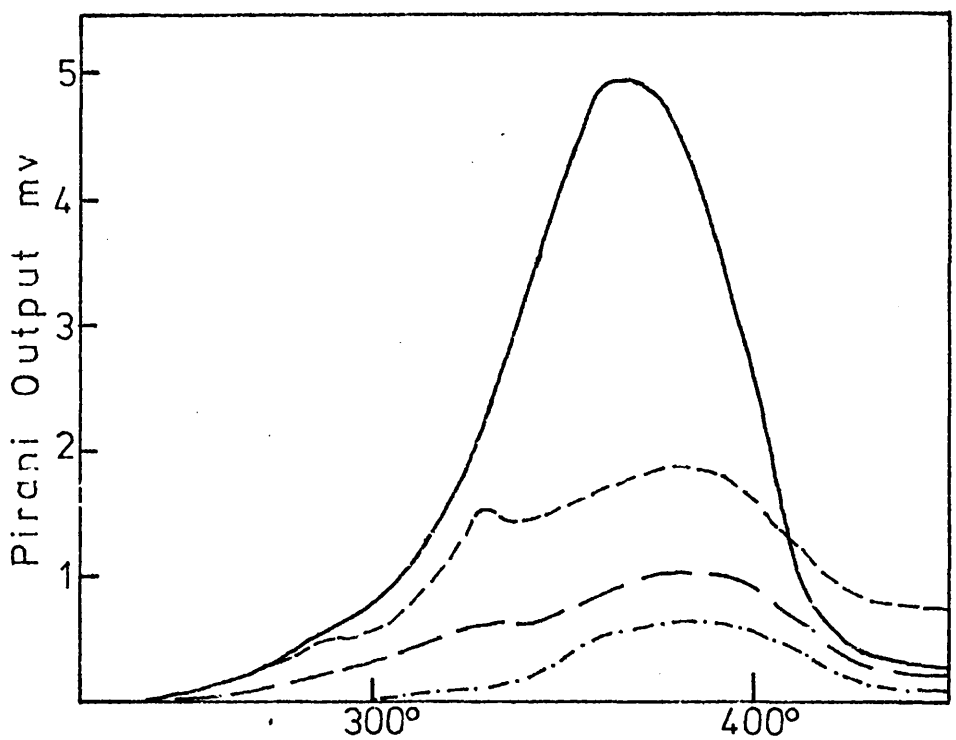


Figure (6.2). TVA curve for the 10% VA-MMA copolymer. Heating rate 10°C/min, 50 mg powder sample.

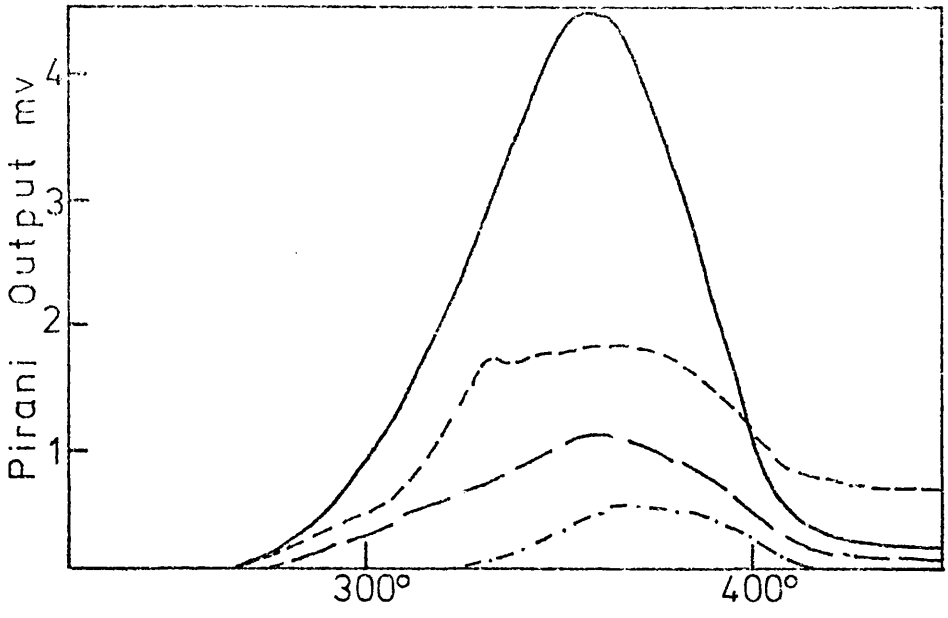


Figure (6.3). TVA curve for the 20% VA-MMA copolymer. Heating rate 10°C/min, 50 mg powder sample.

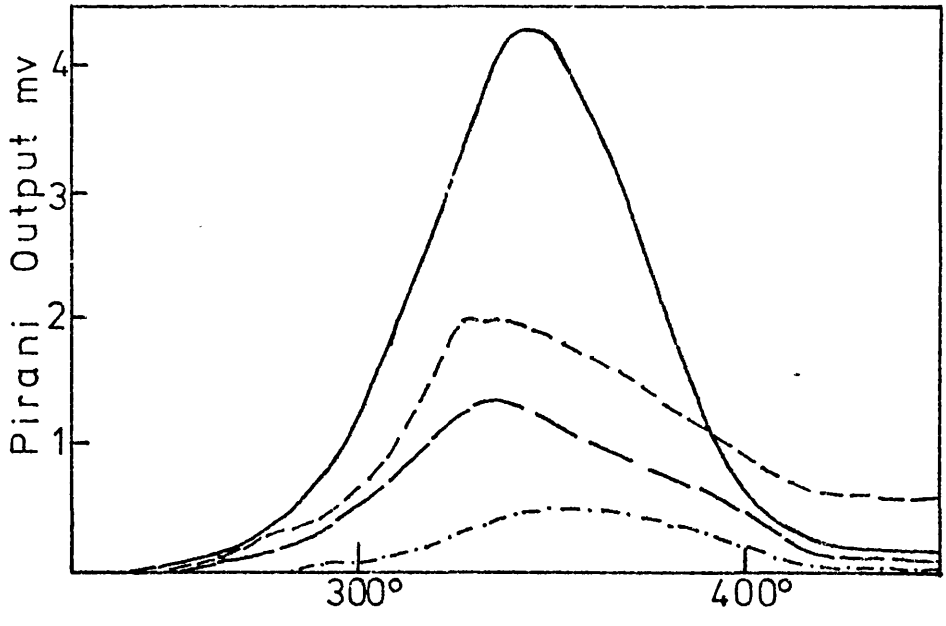


Figure (6.4). TVA curve for the 30% VA-MMA copolymer. Heating rate 10°C/min, 50 mg powder sample.

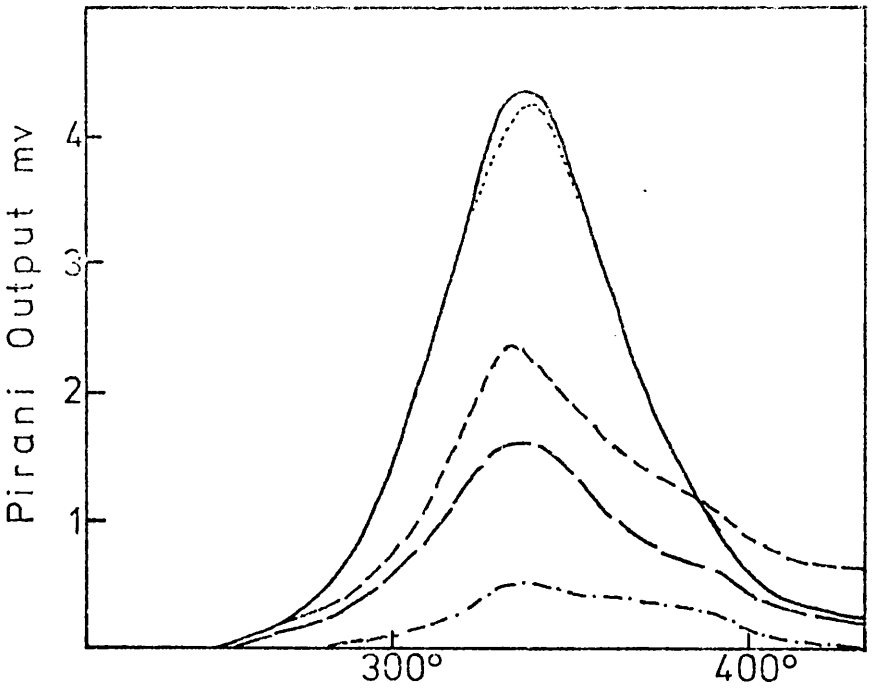


Figure (6.5). TVA curve for the 40% VA-MMA copolymer. Heating rate 10°C/min, 50 mg powder sample.

TABLE 2.

TEMPERATURE OF MAXIMUM VOLATILIZATION RATE FOR POLYMERS IN D.C.T.V.A. THERMOGRAMS

Polymer	PMMA	5%	10%	20%	30%	40%	PVA
$Temp._{max}$	365°	370°	369°	355°	344°	337°	340°

overcoming the first effect.

THERMOGRAVIMETRY.

Figure (6.6) illustrates the weight loss behaviour for the PVA and PMMA homopolymers and for the five VA-MMA copolymers. The curve for PVA is identical to that discussed in an earlier chapter, while that for PMMA shows an initial, slow rate of weight loss consistent with the small amount of chain end initiated depolymerization observed in high molecular weight PMMA samples: at higher temperatures the rate of weight loss increases with the incidence of depolymerization initiated by random scission.

The TG curves for the copolymers indicate that the 5% and 10% copolymers are initially (up to 375°C) slightly more stable than either of the homopolymers, confirming the TVA observations. Also, as the VA content of the copolymers increases, the stability to weight loss decreases, this being confirmed by the TVA behaviour.

DIFFERENTIAL THERMAL ANALYSIS.

DTA data for PVA, PMMA and three copolymers is presented in figure (6.7). PMMA has a large endotherm above 300°C corresponding to depolymerization, while for PVA, deacetylation is shown by the endotherm stretching from 300° to 380°C, and the break-up of the conjugated chains is reflected by an endotherm - exotherm system above 400°C. In the 5% VA-MMA copolymer, the large endotherm due to depolymerization is much reduced, although it has totally disappeared in the 10% copolymer which has no clearly defined exotherm or endotherm. The 30% copolymer shows an endotherm around 300°C corresponding to deacetylation, and also a broad endotherm stretching from 360° to 500°C which is difficult to interpret precisely, although it may be due to both depolymerization and break-up of polyene sequences.

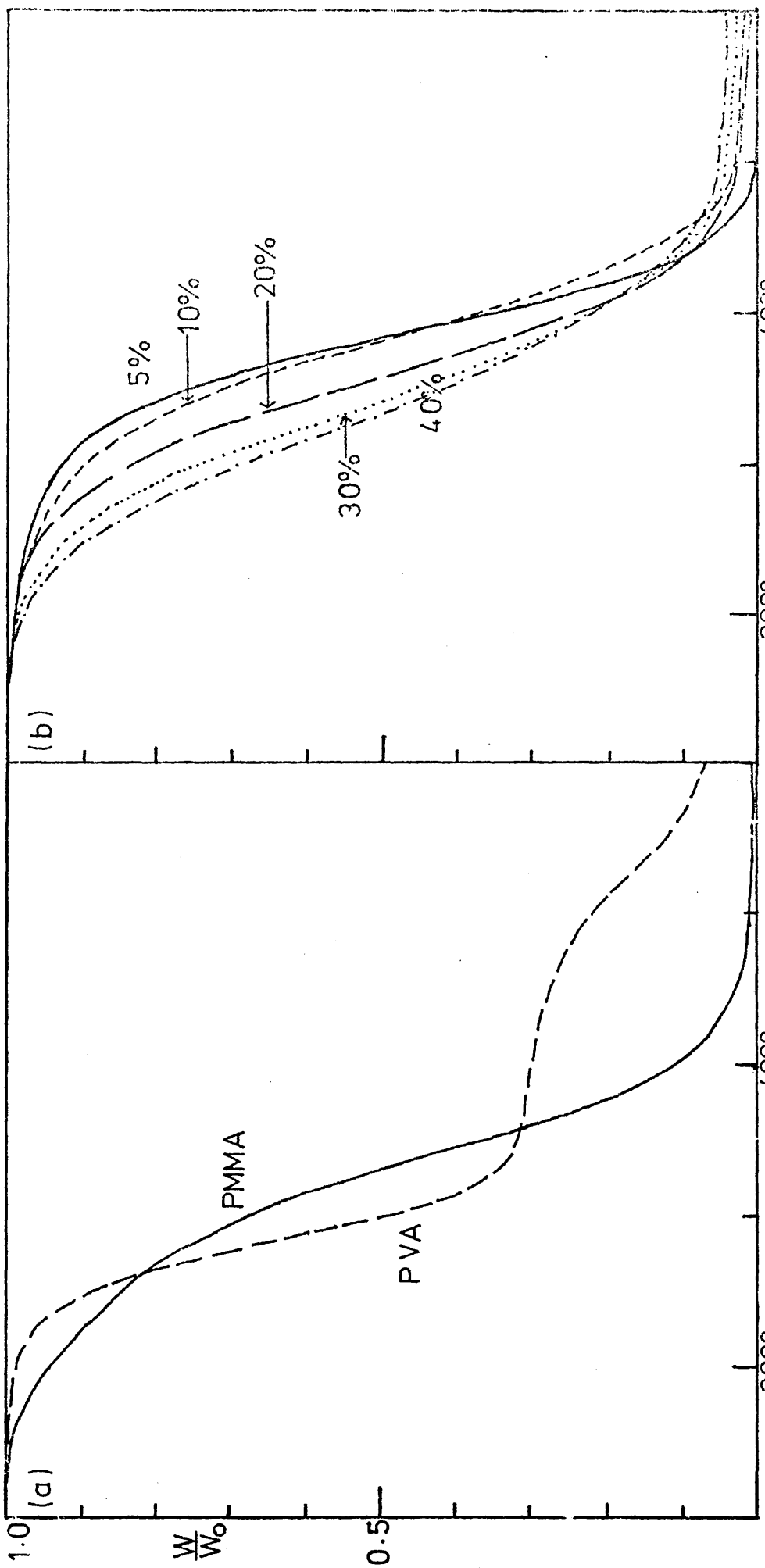


Figure (6.6). TG curves for (a) PVA and PMMA, (b) VA-MMA copolymers. 10 mg samples under N_2. Heating rate $10^{o}C$/min.

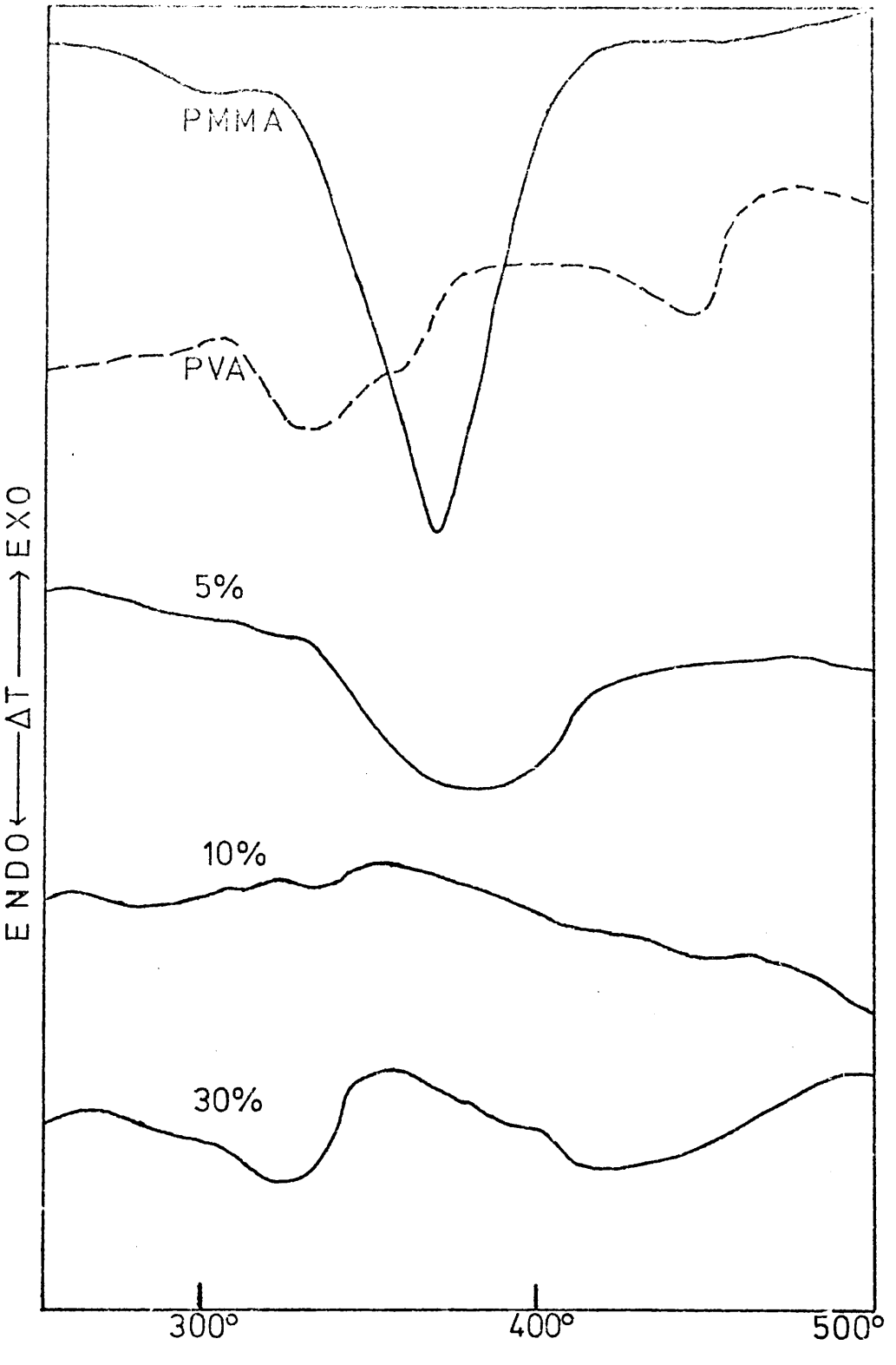


Figure (6.7). D.T.A. curves for PVA, PMMA and three VA-MMA copolymers (5%, 10% and 30%) Sample size 10 mg. Heating rate 10°C/min, under N_2.

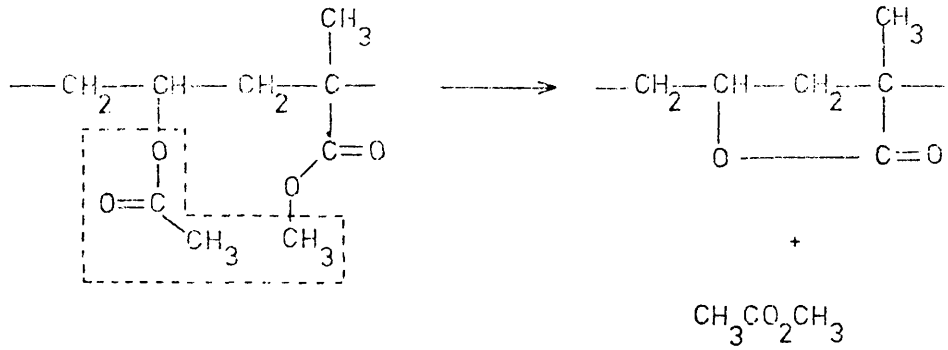
VOLATILES ANALYSIS

Infra-red spectra were obtained of products from degradation at 5°C/min to 425°C of each of the copolymers. It was observed that the fraction condensable at -196°C but non-condensable at -80°C, contained ketene, carbon dioxide and methyl acetate, while the fraction condensable at -80°C contained acetic acid, MMA monomer and methanol. Apart from methanol and methyl acetate, the other products are those obtained from degradation of the homopolymers. Methanol was used as precipitant during purification of the copolymers, and some was retained in the samples, as shown by the presence of a peak at 100°C in the TVA traces. Also, when the products for analysis were collected after this volatilization (observed by TVA) was complete, little or no methanol was detected in the infra-red spectra. The presence of methyl acetate may arise from an interaction of acetic acid with the methacrylate ester groups in a manner similar to that described in chapter three for PVA - PMMA blends.

However, examination of the infra-red spectrum of the cold ring fraction (part of which is reproduced in figure (6.8)), provides an alternative explanation. The spectrum is almost identical to that for the original polymer (as shown for the 40% copolymer), suggesting low molecular weight polymer, apart from an additional peak at 1770 cm^{-1} which is higher than the peaks for absorption due to carbonyl stretching for the acetate ester (1738 cm^{-1}), and the methacrylate ester (1732 cm^{-1}). This (1770 cm^{-1}), is the region of carbonyl absorption for δ -lactones (1780-1760 cm^{-1}), and the shoulder at 1800 cm^{-1} shown in figure (6.8) is in the region (near 1800 cm^{-1}) of absorption of $\beta:\gamma$ unsaturated lactones (76).

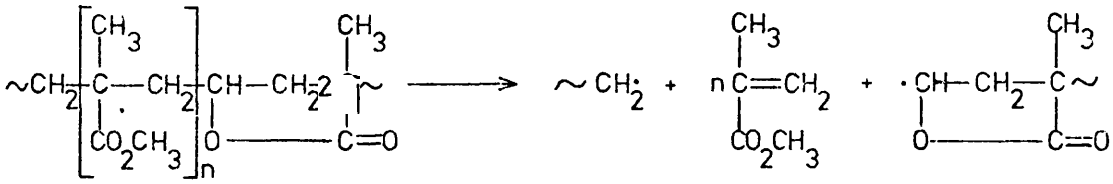
The mechanism of lactonization with subsequent production of methyl acetate is probably similar to that outlined by Zutty and Welsh (19) for lactonization in MMA-vinyl chloride copolymers, which

yields methyl chloride :-

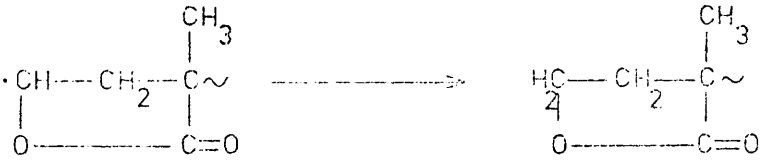


Zutty and Welsh found that at temperatures as low as 150°C, no chain scission took place and cross-linking was absent, confirming that the process was intramolecular rather than intermolecular. Guyot et al (77) have shown that cyclisation of MMA - vinyl chloride copolymers to give methyl chloride is the first reaction to occur on degradation, even preceding loss of HCl. From TVA observations, it was found that this reaction occurred about 200°C; i.e. at much lower temperatures than lactonization in VA - MMA copolymers.

The formation of cold ring fraction in the copolymers may be explained by scission at residual MMA units with subsequent depolymerization, until either a lactone ring or a region of conjugated double bonds is reached. This reaction scheme is outlined below for the case of the lactone ring as blocking unit.

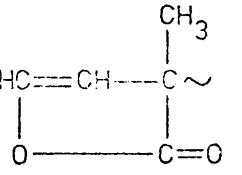


Subsequent disproportionation can result in the saturated γ -lactone (A) or the $\beta : \gamma$ unsaturated γ -lactone (B). It is possible that the α :B unsaturated γ -lactone could be formed, for the carbonyl absorption of these lactones (1760 - 1740 cm^{-1}), (76), will be obscured by the lactone carbonyl absorption and the carbonyl absorptions of the original esters :-



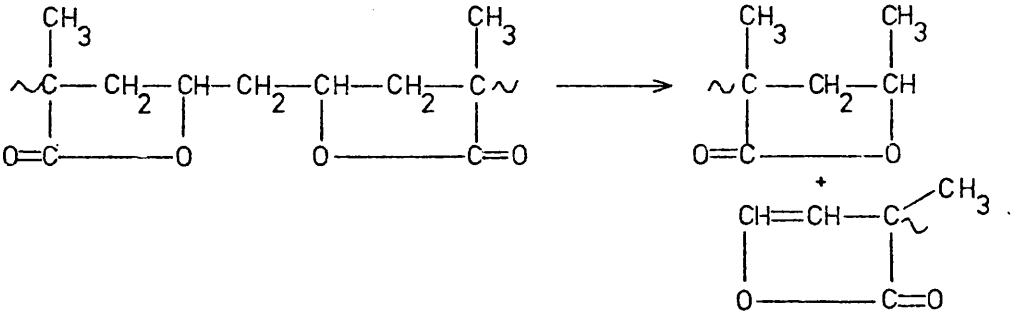
(A)

or



(B)

Another site of chain scission may be the bridging methylene group adjacent to the lactone ring, a situation analogous to that observed by McNeill and Neil (35) in poly (methyl vinyl ketone) and poly (methyl isopropenyl ketone). Breaking of the bond between the methylene group and the adjacent lactone, possibly accompanied by hydrogen transfer, would lead to formation of low molecular weight polymer without concurrent production of volatile material :-



Numerous "isomers" can be obtained after chain scission, depending on the route of hydrogen transfer and on the "configuration" of the adjacent lactone rings: i.e. whether one of the carbonyl groups (or both) are adjacent to the bridging methylene group.

Quantitative analysis of the major liquid products, acetic acid, MMA monomer and methyl acetate was carried out to determine the extent of each of the three major reactions; viz. deacetylation, depolymerization and lactonization. Measurements were made by gas liquid

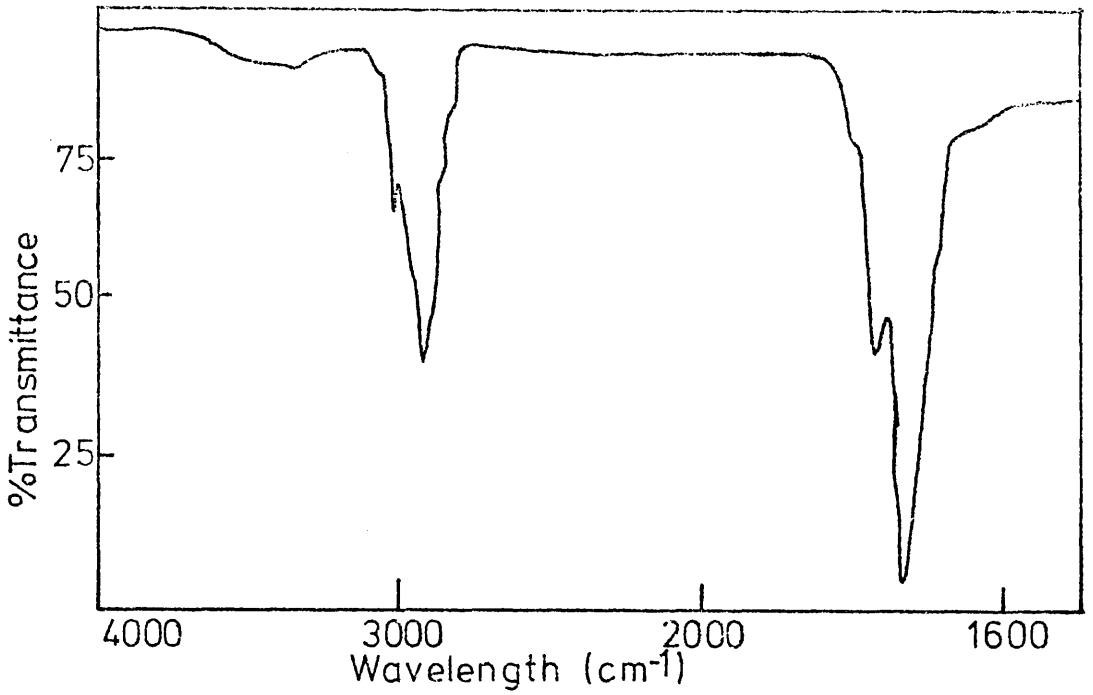


Figure (6.8). Infra-red spectrum of region of interest of the cold ring fraction of the 40% VA-MMA copolymer.

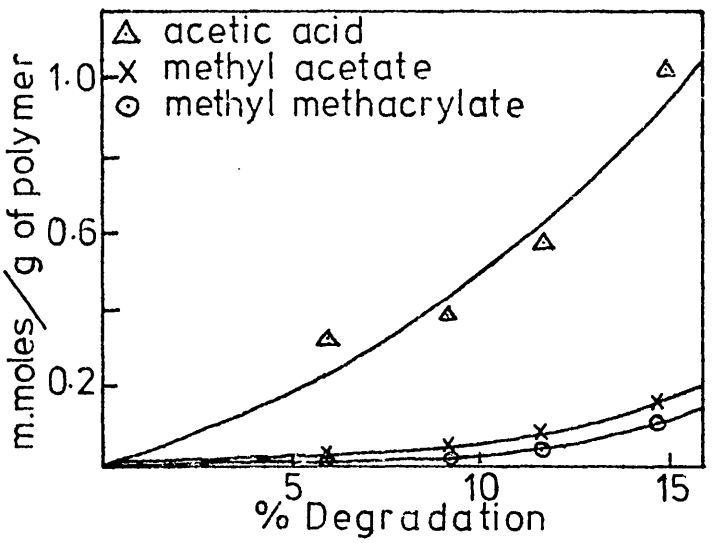


Figure (6.9). Evolution of acetic acid, methyl acetate and methyl methacrylate from degradation at 250°C of the 3% VA-MMA copolymer.

chromatography using the Microtek GC 2000 R Research Gas Chromatograph equipped with a flame ionization detector. A Bentone 34 DNP column was used isothermally at 60°C and the internal standard was cyclohexane.

Table (6.3) shows the amount of each product as a percentage of the total liquid volatiles from degradation at 5°C/min to 500°C, for the 30% and 40% VA-MMA copolymers. For both copolymers, acetic acid is present to the greatest extent in spite of the fact that VA accounts for only 30% and 40% of the composition of the copolymers. MMA monomer accounts for only about 20% of the products, illustrating that depolymerization of MMA units is being suppressed, while lactonization with production of methyl acetate is a minor, but significant reaction in the degradation of both polymers.

TABLE (6.3)

GLC liquid evolution data for two VA-MMA copolymers degraded to 500°C at 5°C/min.

Copolymer / Product	30% VA-MMA	40% VA-MMA
Acetic Acid	70 •4%	63 • 2%
MMA	18 . 9%	20 • 1%
Methyl Acetate	10 •7	16 • 5%

The degradation processes at lower conversions (up to 15%) are shown in figure (6.9) for the 30% copolymer. It illustrates that deacetylation proceeds initially at a rate approximately ten times the rates for depolymerization and lactonization. Thus the initial process in the degradation of the copolymers is deacetylation and this is followed by lactonization and depolymerization which proceed at competing rates. This contrasts with the situation in MMA-vinyl chloride copolymers, in which lactonization is the initial reaction,

completely removing all the MMA or vinyl chloride units (depending on the composition of the copolymer); next dehydrochlorination takes place, followed by depolymerization and break-up of the lactone ring structures at higher temperatures (77).

RESIDUE ANALYSIS.

Investigations of the copolymer residues after partial degradation were undertaken by infra-red spectroscopy, and in figure (6.10), the spectra of the 30% copolymer and its residue after heating at $5^{o}C$/min. to $360^{o}C$ are reproduced. The large peak at 750 cm^{-1} in the spectrum of the undegraded copolymer is due to residual chloroform, from which the films were cast. The degraded copolymer shows a reduction in intensity of all the peaks and the presence of a new peak at 1773 cm^{-1}, attributable to the carbonyl absorption of the δ - lactone. This feature was reproduced in the spectra of partially degraded residues of all the VA-MMA copolymers.

To discover the extent of conjugation in the copolymers, the UV spectra at various extents of degradation for the 30% copolymer were obtained and these are reproduced in figure (6.11). Absorption does not extend much beyond 325 m μ, although the short wavelengths grow more rapidly. The triad centred on 275 m μ (265, 275 and 287 m μ) is due to the 2, 4, 6 - octatriene chromophore which has maxima at 252, 263 and 274.5 m μ in solution in hexane and 260, 270 and 279 m μ in chloroform (78). The lack of absorption beyond the triene region was also observed by Gardner and McNeill (36) for a 33% VA - E copolymer. These workers reasoned that this copolymer contains only 10.9% VA units in groups of more than three, hence the lack of absorption beyond the triene region. In the VA - MMA copolymers, this situation is aggravated by lactonization reaction removing some of the VA units.

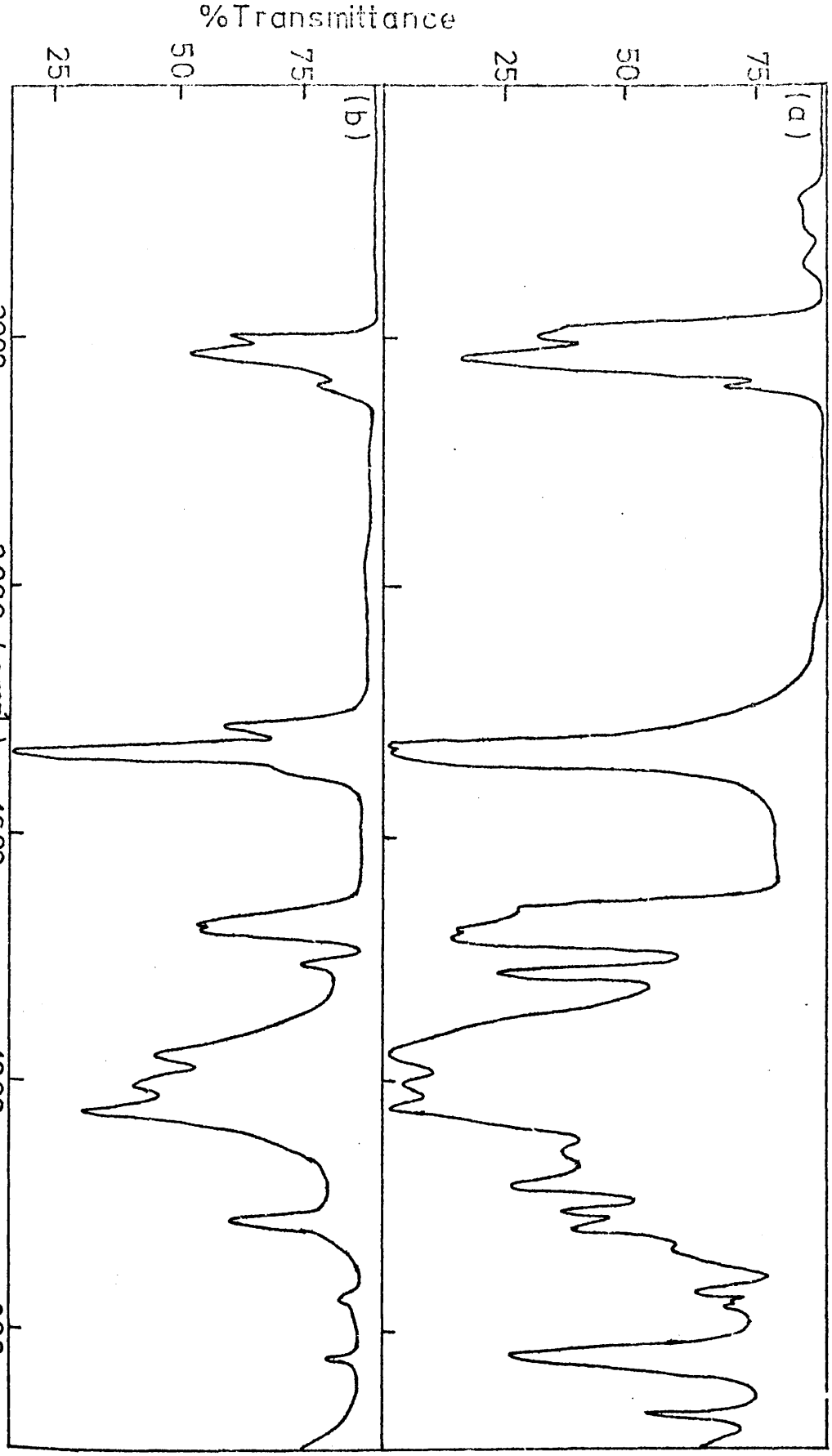


Figure (6.10). Infra-red spectra (a) the 30% VA-MMA copolymer, and (b) the same copolymer heated to 360°C at 5°C/min. Samples as films on NaCl plates.

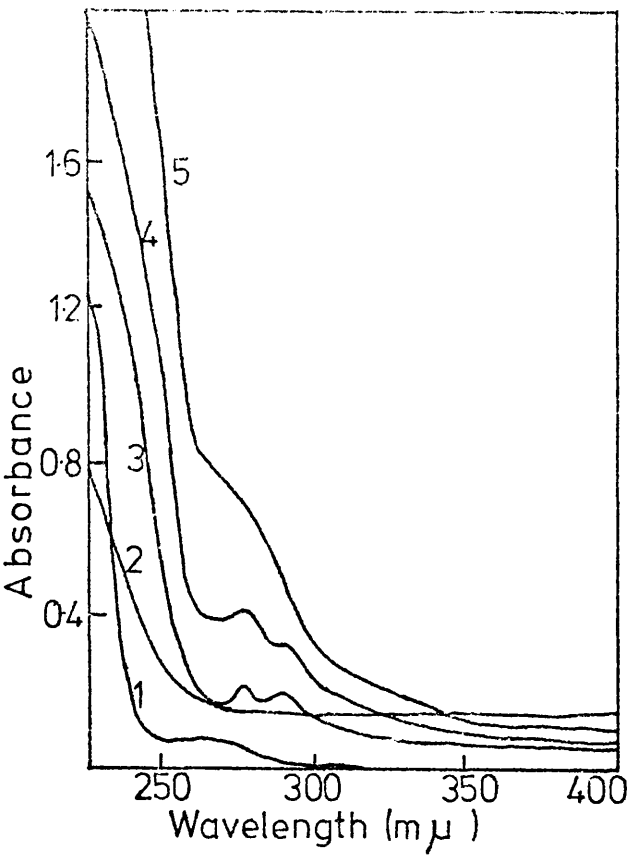


Figure (6.11). Ultra-violet spectra of the 30% VA - MMA copolymer heated at 260°C for ;-
0 min (1), 40 min (2), 70 min (3)
115 min (4), 300 min (5).

The molecular weight behaviour of the 30% copolymer up to 15% degradation is presented in Table (6.4) for isothermal degradation of the copolymers as powder samples at 250°C. As may be seen, the fall in molecular weight is small over this range of decompositon. Also, even at 15% degradation, the copolymers are still extremely soluble, in contrast to PVA which becomes completely insoluble after only 2% weight loss (10). From these facts, it would appear that chain scission and cross-linking are virtually non-existant, and that deacetylation, lactonization and depolymerization are taking place intramolecularly rather than intermolecularly. In this respect, the VA-MMA copolymers are similar to copolymers of MMA and vinyl chloride.

TABLE (6.4)

Molecular weight of the 30% VA-MMA during degradation at 250°C for various lengths of time. 100 mg powder samples.

% Degradation	0	6.0	9.0	11.9	14.8
Mn	92,000	71,500	70,611	75,000	68,500
Mn as % of original	100	78	77	81	75

VA - AN COPOLYMERS (with D. McDONALD).

THERMAL VOLATILIZATION ANALYSIS.

The TVA trace for PAN is shown in figure (6.12) and is similar to that reported previously (13). The major constituents of the initial sharp peak with Tmax 301°C, are NH_3 and HCN. Below 320°C there is no production of material non-condensable at -196°C, indicating that there is no dehydrogenation during the early stages of degradation. In the region 320°C to 430°C, the evolution of volatile material appears as a plateau, the condensable products

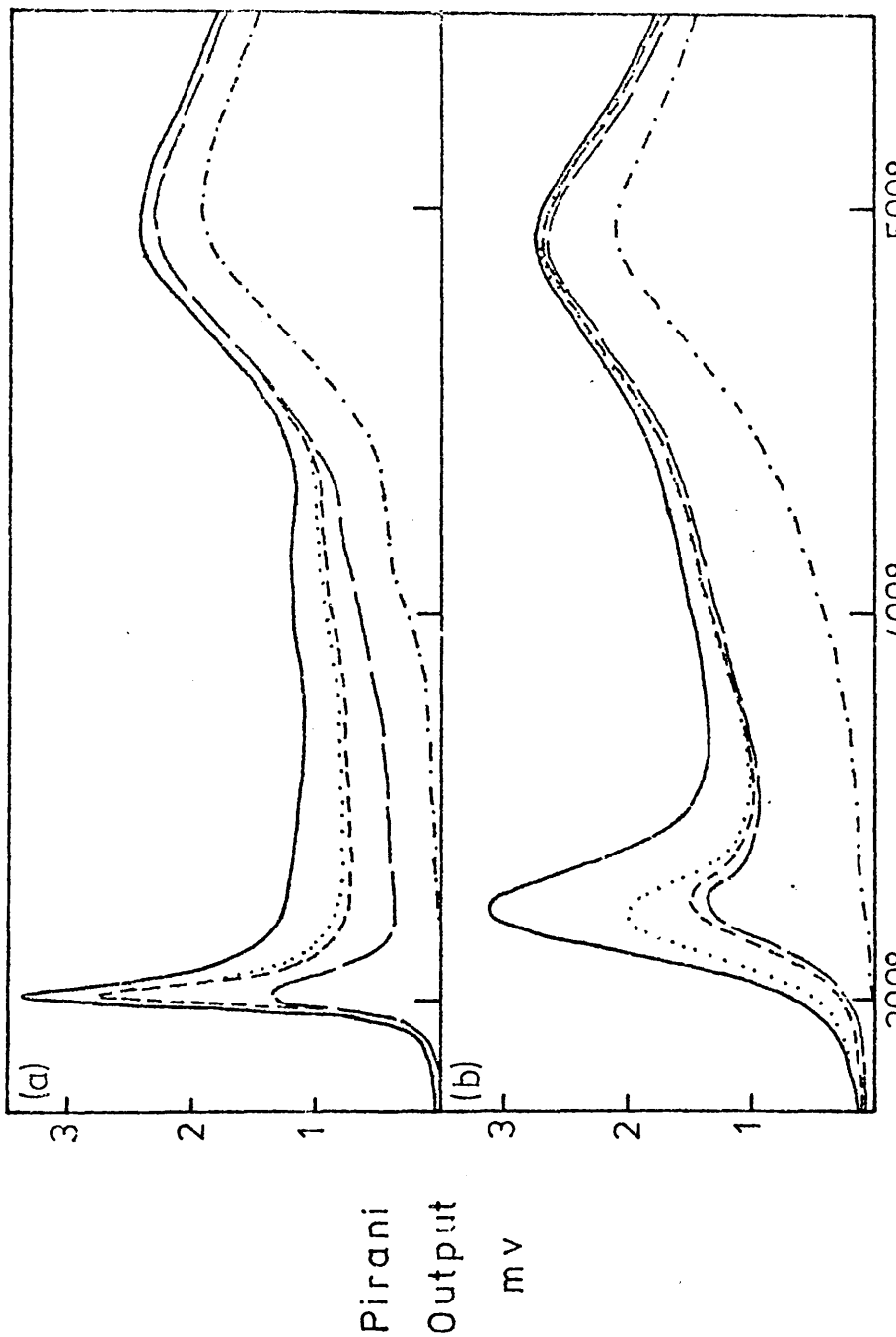


Figure (6.12). TVA traces for (a) PAN, (b) 2% VA-AN copolymer. Sample size 100 mg (powders). Heating rate 10°C/min.

again consisting of NH_3 and HCN. The material forming the peak at 480°C is almost entirely non-condensable at -196°C and it is suspected that hydrogen is being evolved at this stage (13).

The TVA traces for the VA - AN copolymers are reproduced in figures (6.12) to (6.14). The initial sharp peak of PAN is shifted to higher temperatures, and is also broadened, as the proportion of VA in the copolymer increases. The shape and behaviour of the five traces for the cold traps gradually assumes the nature of PVA volatilization behaviour, as the proportion of VA increases (e.g. the limiting rate effect of the -45°C trace). The Tmax values for the four copolymers of higher VA content are in fact greater than that for PVA itself. This suggests that deacetylation in the copolymers is being blocked by AN units or cyclised AN units and this means that each sequence of VA units requires its own initiation step, probably leading to the increased Tmax for deacetylation. The production of volatiles at higher temperatures, consisting mostly of material non-condensable at -196°C from decomposition of AN units, is relatively unaffected. One other factor which may be occurring during decomposition of the copolymers is blocking by VA units, of the AN cyclisation reaction, and this phenomenon too, could lead to an increase in Tmax for the initial peak for evolution of NH_3 and HCN.

DIFFERENTIAL THERMAL ANALYSIS.

The DTA curves for PAN, PVA and three VA-AN copolymers are reproduced in figure (6.15). The curve for PAN has one outstanding feature, viz. a strong and very sharp exotherm of about 17°C, occurring around 300°C, for the thermal cyclisation of nitrile groups (13). PVA exhibits a broad endotherm of less than 1°C in magnitude and this occurs at the temperatures of deacetylation.

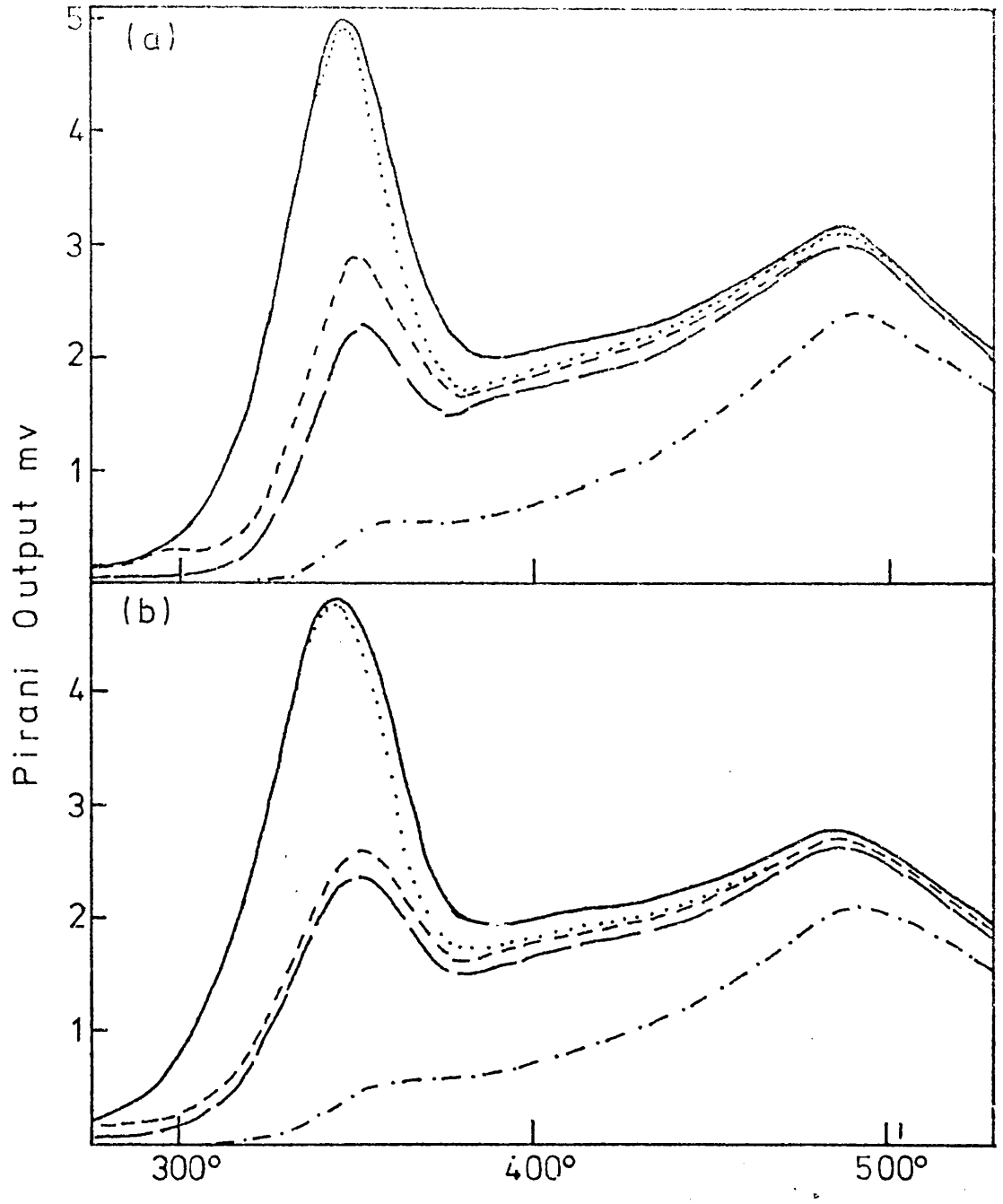


Figure (6.13). TVA traces for (a) 5%, and (b) 18% VA - AN copolymers. Sample size 100 mg (powders). Heating rate 10°C/min.

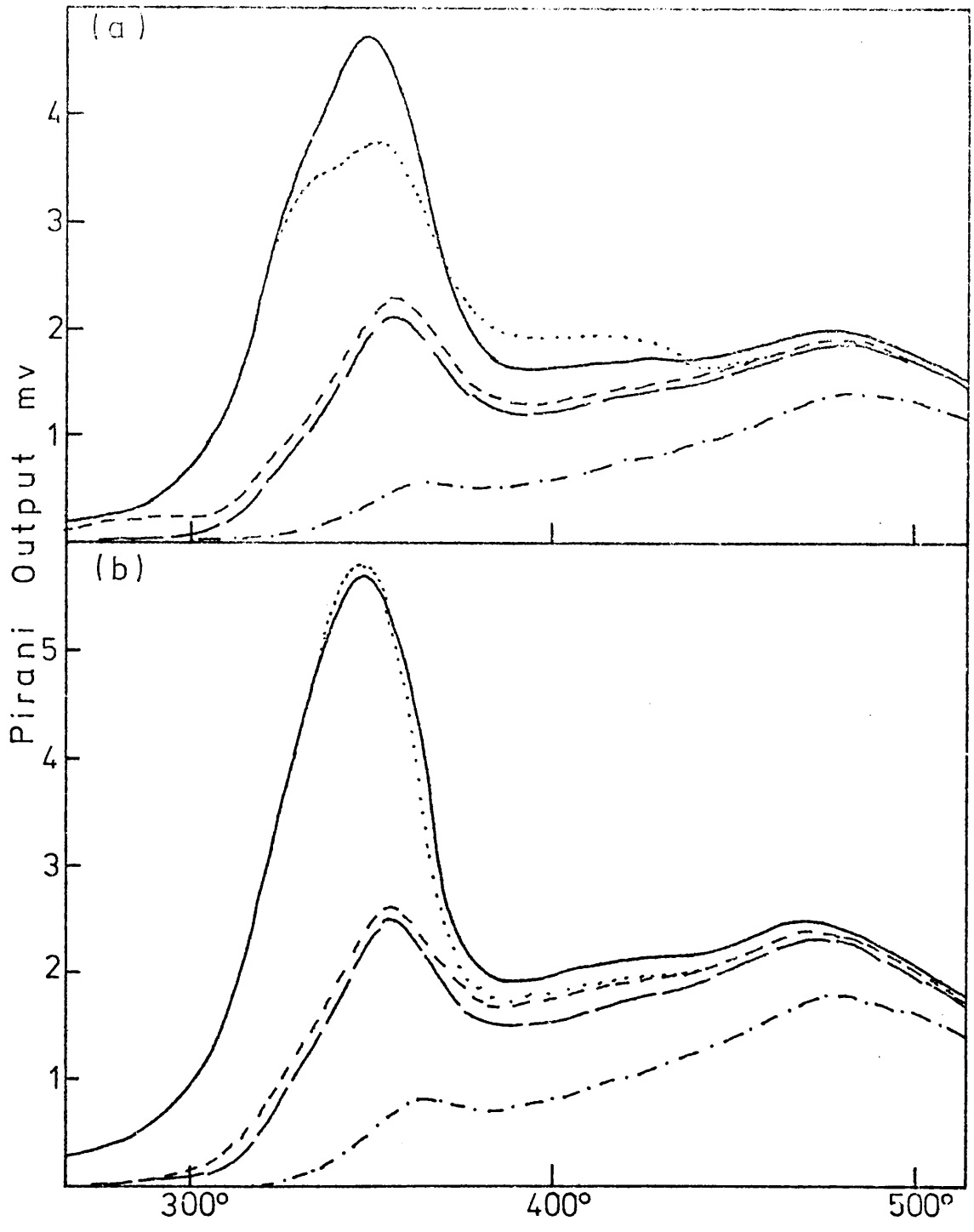


Figure (6.14). TVA traces for (a) 26%, and (b) 41% VA-AN copolymers. Sample size 50 mg (powders). Heating rate 10°C/min.

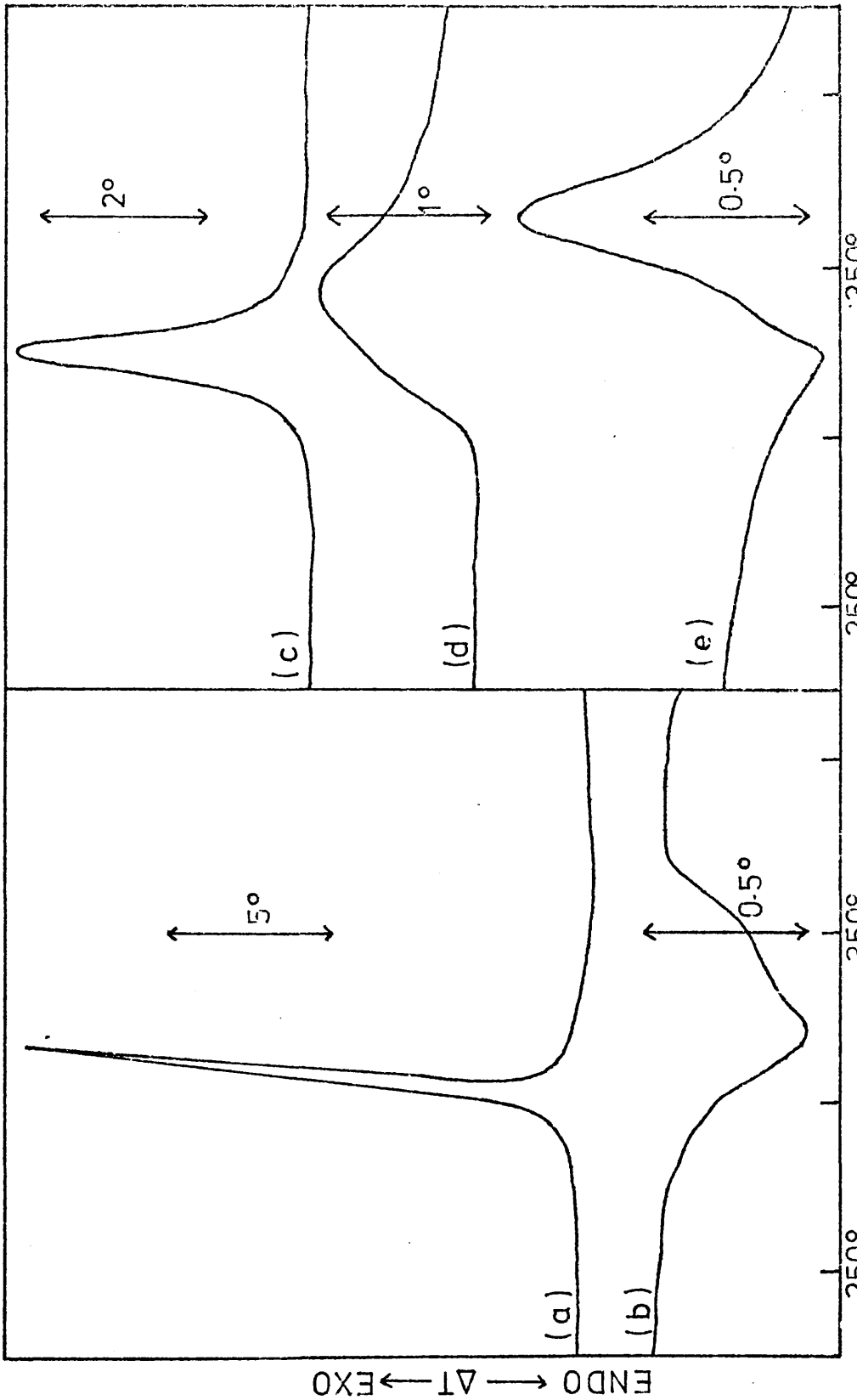


Figure (6.15). DTA curves for (a) PAN, (b) PVA; (c) 2% VA-AN, (d) 18% VA-AN, (e) 41% VA-AN, copolymers. Sample size 10 mg. Heating rate 10°C/min. under N_2.

From the traces for the three copolymers shown, it may be observed that the exotherms are relatively small and occur at higher temperatures than for PAN. Also the 41% copolymer exhibits a small endotherm for deacetylation before the onset of the exotherm. Thus the TVA and DTA investigations produce similar results for the thermal behaviour of the copolymers.

VOLATILES ANALYSIS.

Infra-red spectroscopic analysis of the volatile degradation products revealed, for all the copolymers, ketene, carbon dioxide, ammonia and hydrogen cyanide. The two former products can be associated with deacetylation from VA units, while both the latter products are obtained from AN decomposition. Acetic acid was also observed as a degradation product from all but the 2% and 5% VA copolymers, but it was noted that the yield of acetic acid obtained was less than the theoretical amount expected for a particular VA copolymer composition. Thus, acetic acid is being "removed" from the evolved products, perhaps as suggested (72) by Grassie and McGuchan by reaction with NH_3 to form ammonium acetate which would remain in the cold traps.

RESIDUE ANALYSIS.

Infra-red spectra of the copolymers degraded to 306°C confirmed the observations of Grassie and McGuchan (72) that free nitrile absorptions were still intense after partial degradation, proving that the VA units exert a blocking effect on the nitrile rearrangement. Also, although the acetate carbonyl absorption is reduced in intensity after this degradation process, the frequency remains constant, so that there is no evidence of the acetate unit participating in cyclisation reactions.

VA - S COPOLYMERS.

The TVA curves for PS and the VA - S copolymers are shown in figure (6.15) and as in the case of the VA - MMA copolymers, there is only one peak, indicating that degradation occurs simultaneously in both types of unit in the copolymer. As the VA content of the copolymers increases, the maximum is progressively shifted from 417°C for PS towards 340°C for PVA. The fact that the products of degradation are almost completely condensed at -75°C indicates that the major volatile degradation products are styrene monomer and acetic acid, and that the amount of material non-condensable at -196°C is extremely small.

TG curves for PS and the copolymers are shown in figure (6.17) and these also show a one-stage weight loss process. Also the stability to weight loss parallels the TVA behaviour by decreasing with increasing VA content of the copolymers. For all the copolymers, there is little or no residue at 500°C.

Analysis of the products of degradation (5°C/min to 500°C) by infra-red spectroscopy, revealed small amounts of ketene and carbon dioxide, from the products condensable at -196°C, but non-condensable at -80°C; and acetic acid and styrene from the products condensable at -80°C. This was as expected from the volatiles behaviour in the TVA traces. A brown cold ring fraction was formed during degradation of the copolymers and was found to consist of low molecular weight copolymer containing both VA and S units.

The absence amongst the volatiles of any product other than those obtained from decomposition of the homopolymers, as well as the other evidence from TVA, would seem to indicate that there is no interaction between VA and S units as there is in lactonisation of the VA-MMA copolymers. Deacetylation of the VA units is co-existing with chain scission of the S units which yields monomer and its higher homologues

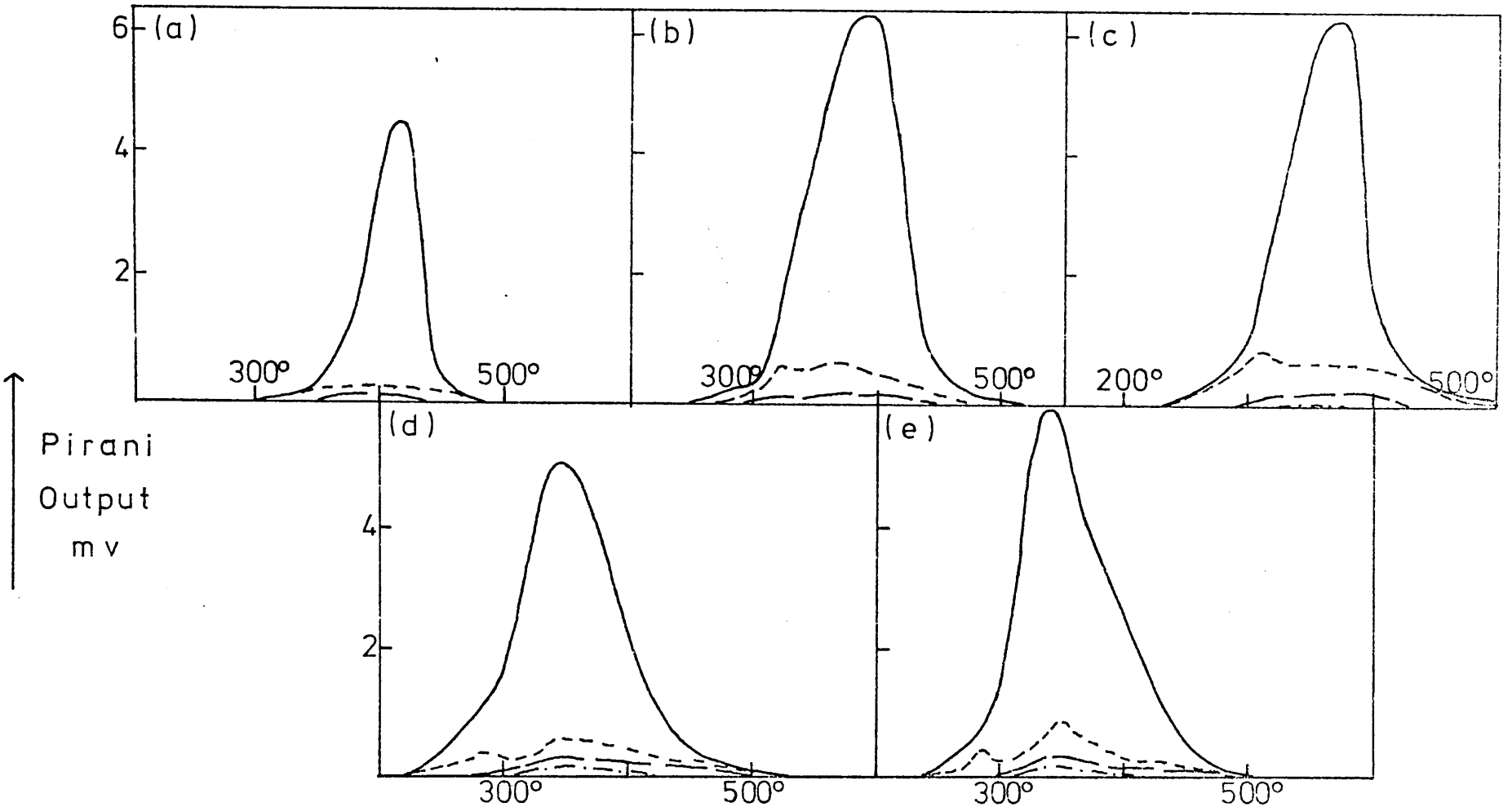


Figure (6.16). TVA traces for (a) PS, (b) 5% VA-S, (c) 10% VA-S, (d) 15% VA-S, (e) 20% VA-S. Sample size 50 mg (powders) Heating rate 10 °C/min.

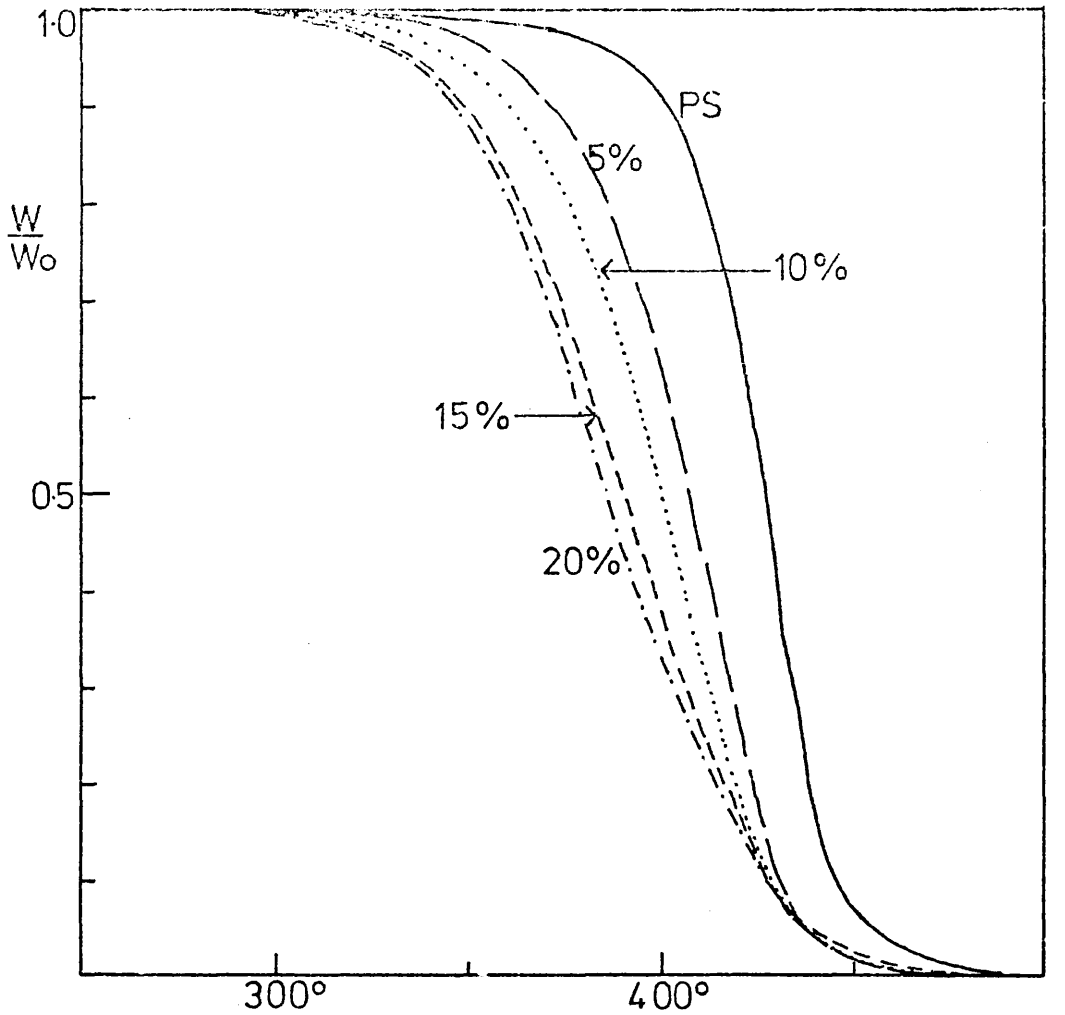


Figure (6.17). TG curves for PS and VA-S copolymers. Sample size 10mg (powders). Heating rate 10 °C/min, under N_2.

as well as short fragments of copolymer.

VA - E COPOLYMERS.

TVA curves for PE and the three VA - E copolymers are shown in figure (6.18). The traces for the VA - E copolymers each show two distinct peaks, corresponding to breakdown of the VA and E units, the latter occurring at higher temperatures. The positions of the two peaks are the same for each of the copolymers, but as the proportion of VA in the copolymer increases, the size of the deacetylation peak also increases. Degradation of the VA units begins at the same temperature as for PVA, but the peak maximum occurs approximately 30^{o}C later, presumably because each short sequence of VA units in the copolymers requires its own initiation step. Another distinctive feature of the TVA curves for the copolymers is the small amount of material non-condensable at -75^{o}, -100^{o} and -196^{o}C evolved during the deacetylation process. This feature was also evident in the TVA traces for the VA - S copolymers.

TG curves for the three copolymers as well as PE are reproduced in figure (6.19). For the copolymers, there are two regions of weight loss. The first stage corresponds to deacetylation of VA unit, the 12%, 18% and 33% VA copolymers losing 9%, 11% and 25% weight respectively (70% weight loss approximately for the proportion of VA). The second stage of weight loss is due to decomposition of the ethylene units. Also, as expected, as the VA content of the copolymers increases, the stability to weight loss decreases.

Infra-red spectroscopic analysis of the products of degradation of the copolymers at 5^{o}C/min showed that the material evolved up to and including the first main peak on the TVA trace, consisted mainly of acetic acid, with traces of ketene and carbon dioxide; while the products evolved from the second peak were acetic acid, ethylene, carbon dioxide, and saturated and unsaturated hydrocarbons. This

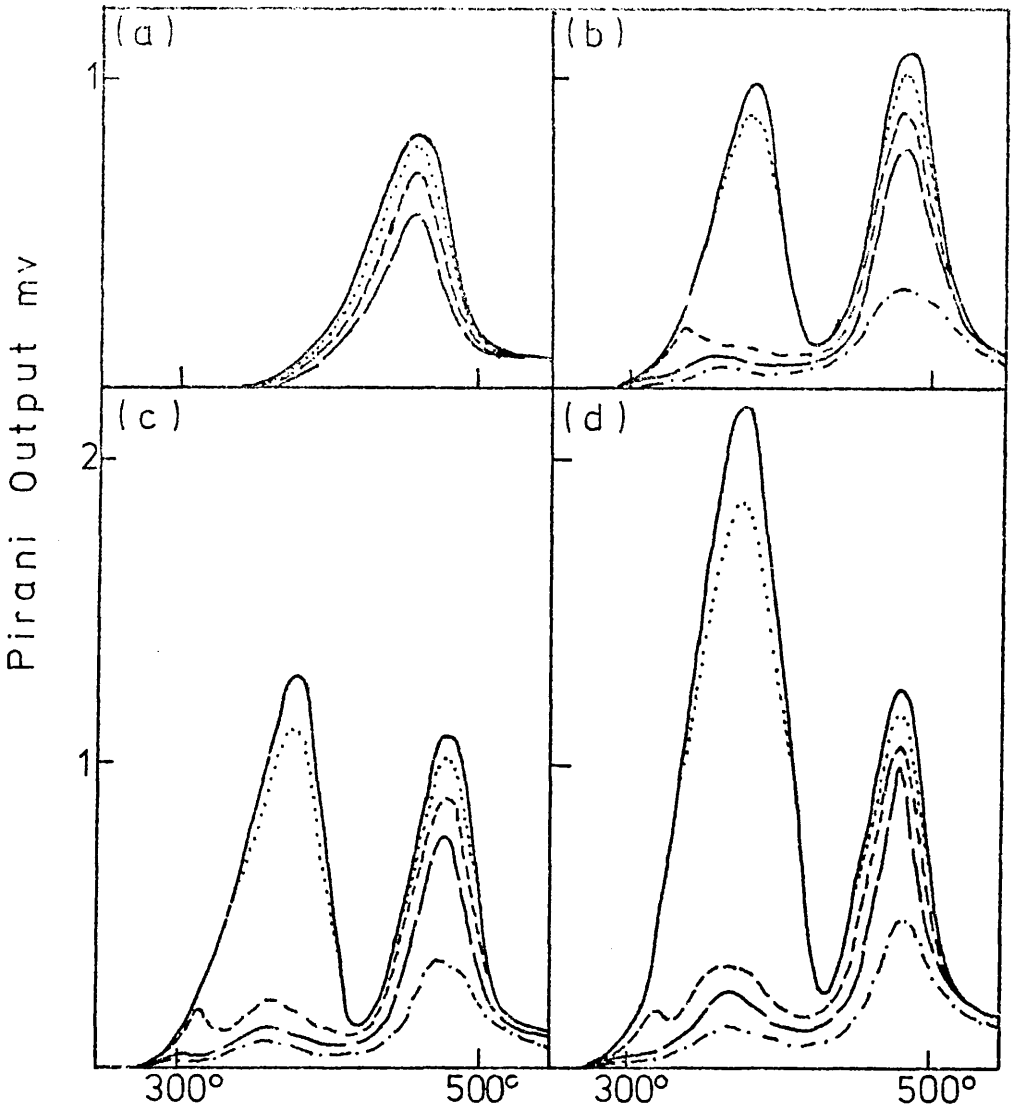


Figure (6.18). TVA curves for (a) PE; (b) 12% VA - E, (c) 18% VA - E and (d) 33% VA - E copolymers. Sample size 100 mg (powders). Heating rate 10°C/min.

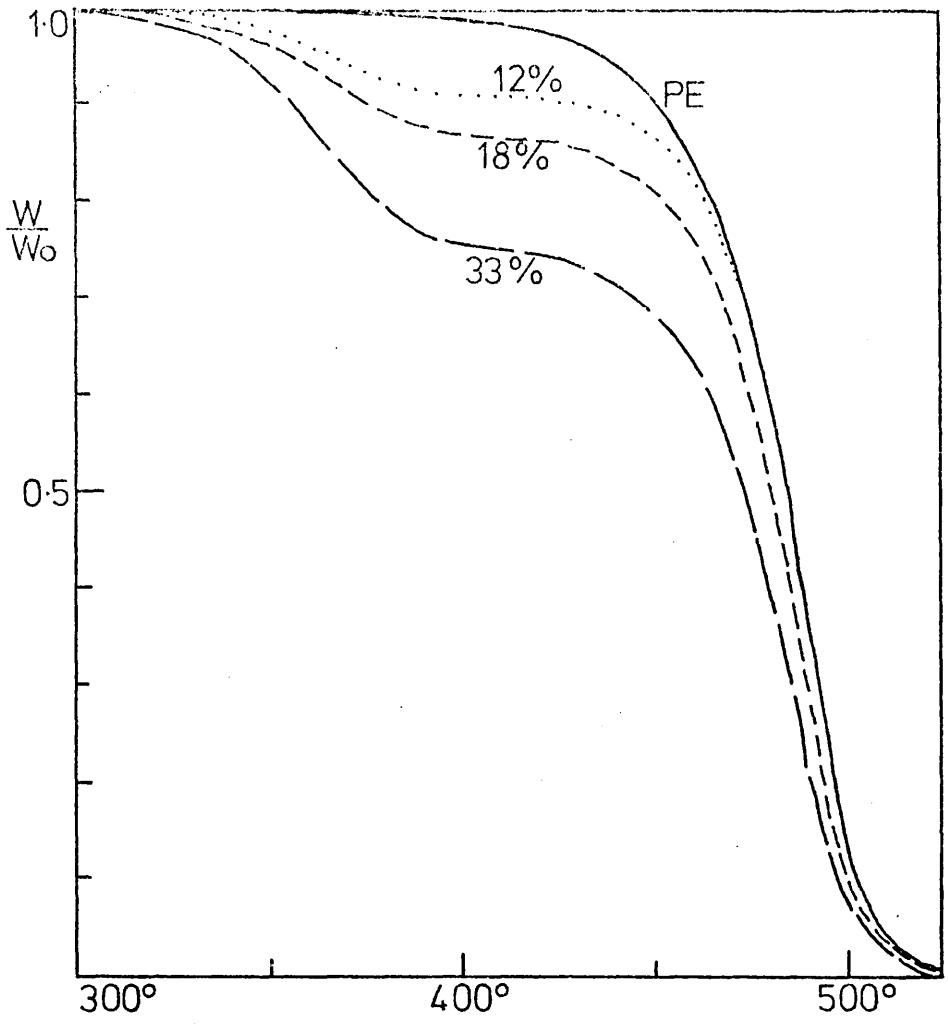


Figure (6.19). TG curves for PE and VA - E copolymers. Sample size 10 mg (powders). Heating rate 10°C/min, under N_2.

confirms the TVA and TG behaviour which indicated two distinct reactions for deacetylation and E decomposition. The cold ring fraction consisted principally of polyethylene type waxes although the carbonyl absorptions of the acetate group were present indicating that the cold ring fraction contained some VA units.

As for the VA - S copolymers, there appears to be no interaction occurring between the VA and the E units during degradation. Deacetylation of the VA units occurs separately and at lower temperatures than chain scission and intermolecular transfer of the E units. Because of the stability of the PE chain, copolymers of VA and E provide excellent materials for studying the reactions of short sections of the PVA chain. The only differences between these short segments of VA in the copolymers and PVA itself are :-

(1) conjugation is limited to triene absorption in the UV (36).

(2) there is less material evolved during deacetylation which is non-condensable at -196°C.

(3) the rate of maximum volatilization occurs at a higher temperature.

CONCLUSIONS.

(1) In VA - MMA copolymers, the presence of VA units inhibits depolymerization of MMA units, and an intra-molecular lactonization reaction occurs between adjacent MMA and VA units, eliminating methyl acetate.

(2) In VA - AN copolymers, deacetylation of VA units co-exists with cyclisation of AN units.

(3) In VA - S copolymers, deacetylation of VA units co-exists with chain scission of styrene units, and evolution of styrene monomer.

(4) In VA - E copolymers, deacetylation of VA units proceeds

separately from and at lower temperatures than decomposition of the E units.

(5) In the VA - AN, VA - S and VA - E copolymers the Tmax for deacetylation is higher than in PVA, since each short VA sequence requires its own initiation step.

CHAPTER SEVEN

THE DEGRADATION OF POLY (VINYL ACETATE).

INTRODUCTION.

In the preceding chapters, some aspects of the degradation of PVA have been discussed. In this chapter the decompositon of PVA will be reviewed in the light of these results, and those of other authors.

As previously discussed, Grassie's view (9) of the degradation of PVA, published in the early fifties, is still accepted in principle. This applies to the basic conclusion that the process of elimination of acetic acid is a chain reaction, initiated by the loss of the first molecule of acid and by the formation of at least one double bond, which facilitates the elimination of further molecules.

THE INITIATION PROCESS.

Greater changes have been observed in the conception of initiation since Grassie's ideas (9) that the initiation step consists in the elimination of a molecule of acetic acid from the saturated chain, either directly from its end, or from places close to the end. Zimmermann (47) proposed that the first step also consists in the elimination of acetic acid, which, however, proceeds statistically. Servotte and Desreux (10) observed no difference in rate among samples having considerably different molecular weights (8,000 - 800,000), in contradiction to the hypothesis of initiation of degradation at the end of chains.

In the present work, the rates of deacetylation of the three PVA samples described in chapter three were investigated by TVA and by estimation of acetic acid evolution by titration with standard alkali.

The history and preparation of each PVA sample was different and the molecular weights varied from 37,100 for PVA (BDH) to 301,000 for PVA I and 356,000 for PVA II.

TVA traces for each of these samples were obtained at $5^{o}C$/min. 50 mg film samples (cast from benzene) were degraded using the same TVA tube and the degradations were performed in triplicate for each polymer. It was observed that the initiation temperature fell within a $1^{o}C$ range (271^{o} - $272^{o}C$) for the three samples and the Tmax within a $2^{o}C$ range (324^{o} - $326^{o}C$). Similar results were obtained for the samples degraded as powders.

The estimation of acetic acid from isothermal degradation at $234^{o}C$ of the three PVA samples in the form of 40 mg films is shown in Table (7.1), and it may be observed that although there are small differences in the absolute values obtained, there is no direct relationship between the amount of acid produced and the inverse of the molecular weight as observed by Grassie (9).

These results suggest initiation of deacetylation occurs randomly throughout the chain, not at chain ends. Random initiation of acetic acid loss can also explain why polyene sequences with a maximum number of double bonds equal to twelve are observed spectroscopically in degraded PVA (47); although a view prevailed for a long time that the kinetic length of the chain of elimination can equal the degree of polymerization, being limited only by structural irregularities of the macromolecular chain (9). Production of a double bond in the polymer chain by initial acetic acid loss facilitates the elimination of an adjacent acetic acid molecule, and a similar allylic activation is still efficient in the next steps, but becomes smaller the longer, and the more stabilised by resonance the adjacent sequence is. At a particular length, the energy

TABLE (7.1)

Production of acid (as % deacetylation) from isothermal degradation at 254°C of the three PVA samples for 80 and 200 min.

Sample	80 min.	200 min.
PVA (BDH)	1.48	3.92
PVA I	1.05	3.38
PVA II	1.35	3.36

required for the elimination of another molecule of acetic acid exceeds the energy gain resulting from the formation of a more conjugated system, and the growth of the polyene sequence finishes (56). Another possible explanation of this phenomenon will be given later in this chapter.

RATES OF DEGRADATION.

Some considerable discrepancies exist between the absolute values of rates of deacetylation obtained by Grassie (9) and Servotte and Desreux (10). Also the kinetic scheme proposed by Grassie gives a rate of formation of acetic acid which is directly proportional to time, but the latter workers observed that this rate was proportional to $(\text{time})^{0.25}$.

Isothermal degradations were carried out on 10 mg powder samples of PVA (BDH) using the Du Pont thermobalance. Figure (7.1) shows the weight loss at various times for degradation temperatures between 245° and 288°C. Using this data, attempts were made to find the order of the decomposition reaction by the function method (79). However, this was not successful since fairly good agreement was obtained with this data, for $1/2$, 1st, $3/2$ and 2nd orders at low conversions, while at higher conversions, good agreement was achieved for $1/2$ and 1st orders.

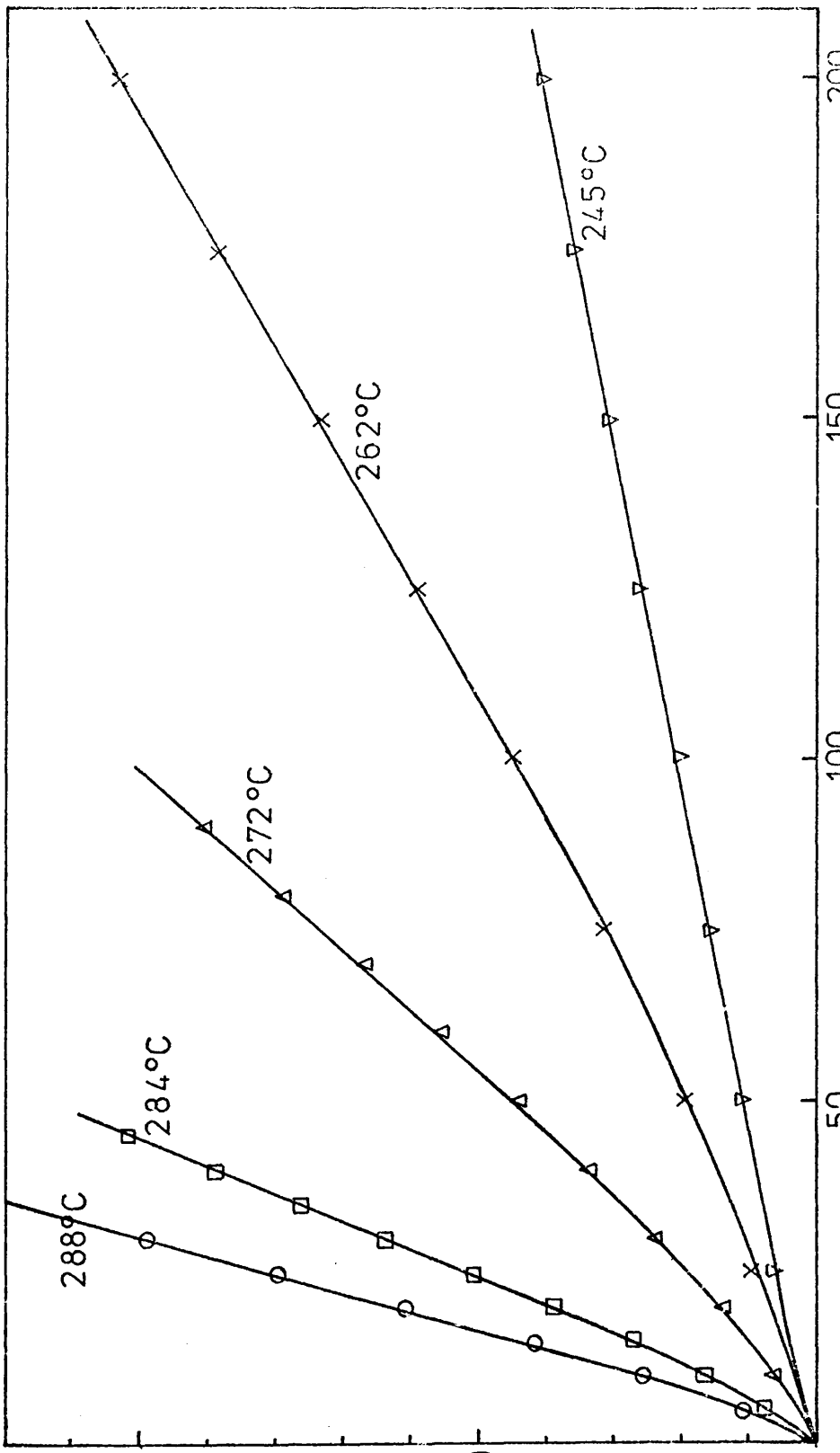


Figure (7.1). Weight loss behaviour for isothermal degradation of 10 mg powder samples of PVA (BDH) under N_2 at 245°, 262°, 272°, 284° and 288°C.

Differential plots of $\log \frac{-dC}{dt}$ against $\log C$ can lead to values for the order of the reaction, if the reaction proceeds without complexity (79);

$$-\frac{dC}{dt} = k\,C^{n}$$

$$\log\left(-\frac{dC}{dt}\right) = \log k + n \log C \quad .$$

If, on the other hand, the plot exhibits curvature (as it did in the case of PVA (BDH)), then the reaction has some complicating feature and does not have a simple order (79). Thus it appears that the decomposition of PVA is not a simple reaction following a simple order, but is complex, probably with a reaction order which changes with extent of reaction.

The activation energy, E, and pre-exponential factor, A, were determined by applying the Arrhenius equation,

$$k = A\,e^{-E/RT}$$

to the logarithm of the initial rates (up to 10% reaction) of figure (7.1). A graph was made of log (initial rate) vs (absolute temperature)$^{-1}$, shown in figure (7.2), and the best line and standard deviation of the gradient and intercept were calculated by the least squares method. From the gradient and intercept,

$$E = 37.9 \pm 2.0 \text{ k.cals/mole}$$

$$\log A = 14.6 \pm 0.8$$

This compares well with the value of 40 k.cals/mole obtained by Servotte and Desreux (10).

PYROLYSIS OF "MODEL" COMPOUNDS.

The decomposition of low molecular weight acetates in the gas phase has been investigated by Chytry et al (80). It should be borne in mind that there might be changes in the mechanism of the reaction

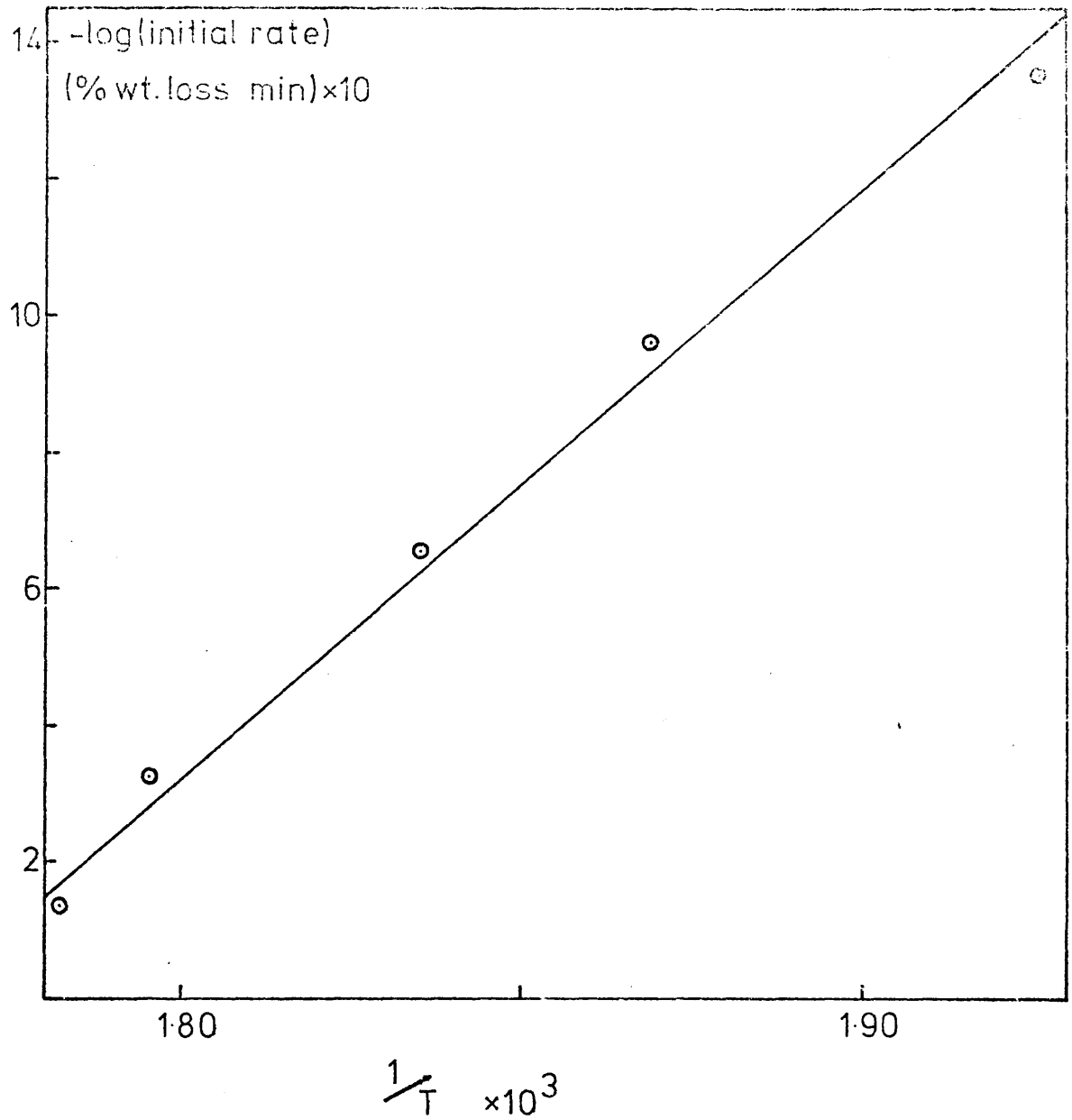


Figure (7.2). Plot of - log (initial rate) vs $1/_T$ x 10^3 for isothermal weight loss from PVA (BDH).

during the transition from the gas phase to the solid phase, and also that a certain risk is connected with the extrapolation of values from the temperature region in which these pyrolyses were followed, to the low temperature region used in investigations of the decomposition of PVA.

(a) Models of the saturated chain.

The mean values for the activation energy of decomposition of primary, secondary and tertiary acetates were found (80) to be 48, 45 and 38 k.cals, whereas for chlorides (18) they are respectively, 56, 50 and 45 k.cals, and yet PVA has a considerably higher thermal stability than PVC. For PVC, the differences between the models of an ideal polymer structure and the polymer itself, are so marked, that it is impossible not to draw a conclusion about the existence of labile sites in the polymer from which the chain "zip" dehydrochlorination sets in. The values for elimination of acetic acid from acetate "models" for PVA argue against the assumption (9) that initiation occurs preferentially on saturated end groups, and suggests that initiation could occur statistically inside an ideal PVA chain.

Also, no difference was observed (80) in the stability of meso and racemic "models" (like 2, 4 - diacetoxypentane), and since these may be regarded as simplified "models" of isotactic and syndiotactic polymer respectively, there is no reason to expect any difference in the thermal stabilities of the respective polymers.

(b) Models of the unsaturated chain.

Elimination of the first acetic acid molecule from a regular PVA chain results in the structure,

$$\sim CH_2 - \underset{\underset{OAc}{|}}{CH} - CH = CH - CH_2 - \underset{\underset{OAc}{|}}{CH} - CH_2 \sim$$

which can theoretically eliminate two acetoxy groups; a group with a hydrogen atom of the allyl-activated methylene group, and a group at the allyl - activated carbon atom. As shown by results from the "models" 4-acetoxy-1-pentene and 4-acetoxy-2-pentene(80), the latter case is more likely to occur, in contrast with what has been proposed by Grassie (9) and Zimmermann (47).

Results from these systems also contribute to elucidation of the problem why polyene sequences with a maximum of twelve double bonds are detected in degraded PVA. The ratio of the rate constants for elimination of acetic acid from a "model" of the ideal structure and from a "model" in which the acetate group is allyl-activated by two double bonds is 1:14 at 200°C (80). Thus in a macromolecule in which the chain elimination is already taking place, random elimination is also likely to occur in the above ratio. This is how further chains start, which for the original chain represents a structural irregularity, leading to its premature termination and disturbance of conjugation of the polyene system.

SUMMARY OF THE MECHANISM OF DEACETYLATION OF PVA.

(1) The degradation of PVA results in loss of acetic acid by a chain reaction, which is initiated at random in the polymer molecule by the loss of the first acetic acid molecule and the formation of at least one double bond, thus facilitating the elimination of further molecules by allylic activation.

(2) Because of the random nature of the initiation process, the kinetic chain length of deacetylation reaches a maximum after formation of approximately twelve double bonds.

(3) The observation, in blends with PMMA (chapter three) and with polypropylene (25), that radicals are formed during PVA degradation, suggests that a radical mechanism is in operation.

This probably involves thermal scission of C - O bonds as the initiation step, forming an acetate free-radical in a manner suggested by Madorsky (2). Abstraction of hydrogen atoms by acetate free-radicals may also take place intermolecularly, resulting in cross-linkages and insolubility of the polymer residue (10).

(4) The formation of volatile products besides acetic acid during PVA degradation occurs by decomposition of acetic acid to ketene, water, CO_2 and CH_4, and also by secondary decomposition of ketene itself (see chapter five).

(5) The subsequent reaction of the polyene sequences at higher temperatures probably occurs by a Diels-Adler type reaction (48, 49), as described in chapter three.

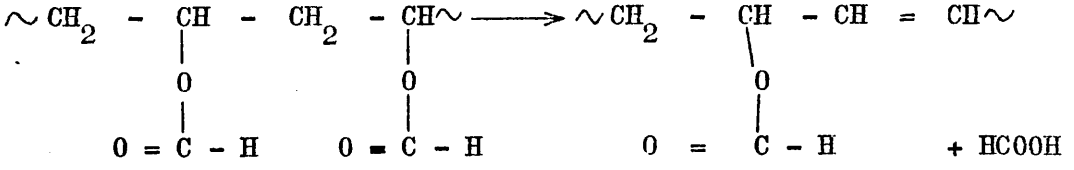
CHAPTER EIGHT

THE DEGRADATION OF POLY (VINYL FORMATE).

INTRODUCTION

It might be expected that poly (vinyl formate) (PVF), being the lower ester homologue of PVA, would degrade in a similar fashion to PVA, and previous brief studies have verified this (36, 71). On degradation this polymer produced UV spectra, which were indistinguishable from those for PVA (36), indicating that some form of elimination reaction is taking place, yielding a residue of conjugated polyene sequences. PVF is, however, thermally less stable than PVA, and the TVA curves are quite different to those for PVA. in that the peak for the elimination reaction with its Tmax at 273°C is at first almost entirely composed of material non-condensable at -196°C, and later has a shoulder which is composed partly of condensable material (36).

By analogy with PVA, the expected degradation product from the elimination reaction (shown below) is formic acid



Thermogravimetry showed a 64% weight loss in a single stage reaction commencing at 230°C and reaching completion at 375°C; this weight loss corresponds to quantitative loss of formic acid from the polymer. Formic acid was detected amongst the volatile products along with quantities of CO, CO_2 and CH_4 (36).

POLYMERS USED.

The preparation and molecular weight determinations of these polymers formed part of the work undertaken for a thesis for the

BSc degree.

Commercial vinyl formate (twice distilled) was polymerised in bulk, AIBN, and UV radiation being used for initiation. The polymers were reprecipitated in methanol from acetone solution, and dried under vacuum. Number-average molecular weights were obtained by calculation (81) from viscosity measurements in acetone at 30°C. Details of the polymer samples are given in Table (8.1).

TABLE (8.1)

Poly (vinyl formate) Samples

Sample	History	$\bar{M}n$
PVF (I)	Bulk polymerization at 60°C. 0.25% AIBN	23,000
PVF (II)	" " " " 0.10% AIBN	71,000
PVF (III)	" " " 0°C. 0.1% AIBN/UV	170,000
PVF (IV)	" " " " 0.1% AIBN/UV	90,000

R E S U L T S.

Thermal Volatilization Analysis.

The TVA trace for PVF (III) is shown in figure (8.1) and is basically similar to that obtained previously (36); viz, two peaks with maxima at 262° and 321°C. The reaction begins at about 190°C and at the first peak, the products are almost entirely non-condensable at -196°C. At the second peak the divergence of the traces shows that condensable material is being formed. Formic acid is non-condensable at 0° and -45°, but completely condensed at -75°C in the TVA apparatus, and thus there must be other products evolved at this stage also.

In spite of the differences in preparation and molecular weight, all the samples gave similar TVA traces when degraded as films. When the polymers could be easily ground and hence evenly spread over the base of the TVA tube, the TVA traces for the films and powders were

almost identical, but PVF (II) was not easily grindable and the trace of the solid sample differed somewhat from that for the film sample. This suggests that the volatilization behaviour of PVF during degradation in the TVA apparatus may be to a certain extent dependent on the sample form. Indeed, it was observed that for the same weight of polymer as the surface area of the film increased, so did the amount of formic acid produced from vacuum degradation at 264°C.

Thermogravimetry and Differential Thermal Analysis.

The TG curve, reproduced in figure (8.2) shows the initial single-stage weight loss (64%) which corresponds to complete deformylation. The weight loss at higher temperatures corresponds to break-up of the conjugated polyene chains as for PVA and PVC. The DTA curve, also reproduced in figure (8.2), shows an endotherm, of 1°C, associated with this formic acid elimination reaction, and which is similar to the endotherm obtained during deacetylation of PVA.

Estimation of Formic Acid Production

Powder samples of PVF were degraded at 330°C under vacuum for one hour, during which time the total volatilization associated with the elimination process had occurred to completion, and the residue was yellow-brown in colour. The volatiles which had been condensed were titrated with standard NaOH using phenolphthalein as indicator, and the results revealed that the amount of formic acid obtained from degradation at this temperature was equivalent to 69% of the "theoretically" available amount. This suggests that of the initial 64% weight loss from PVF, only 44% is formic acid, the other products (CO_2, CO and CH_4) accounting for the remaining 20% weight loss.

Kinetics of Deformylation.

Isothermal degradations were carried out on 10 mg powder samples

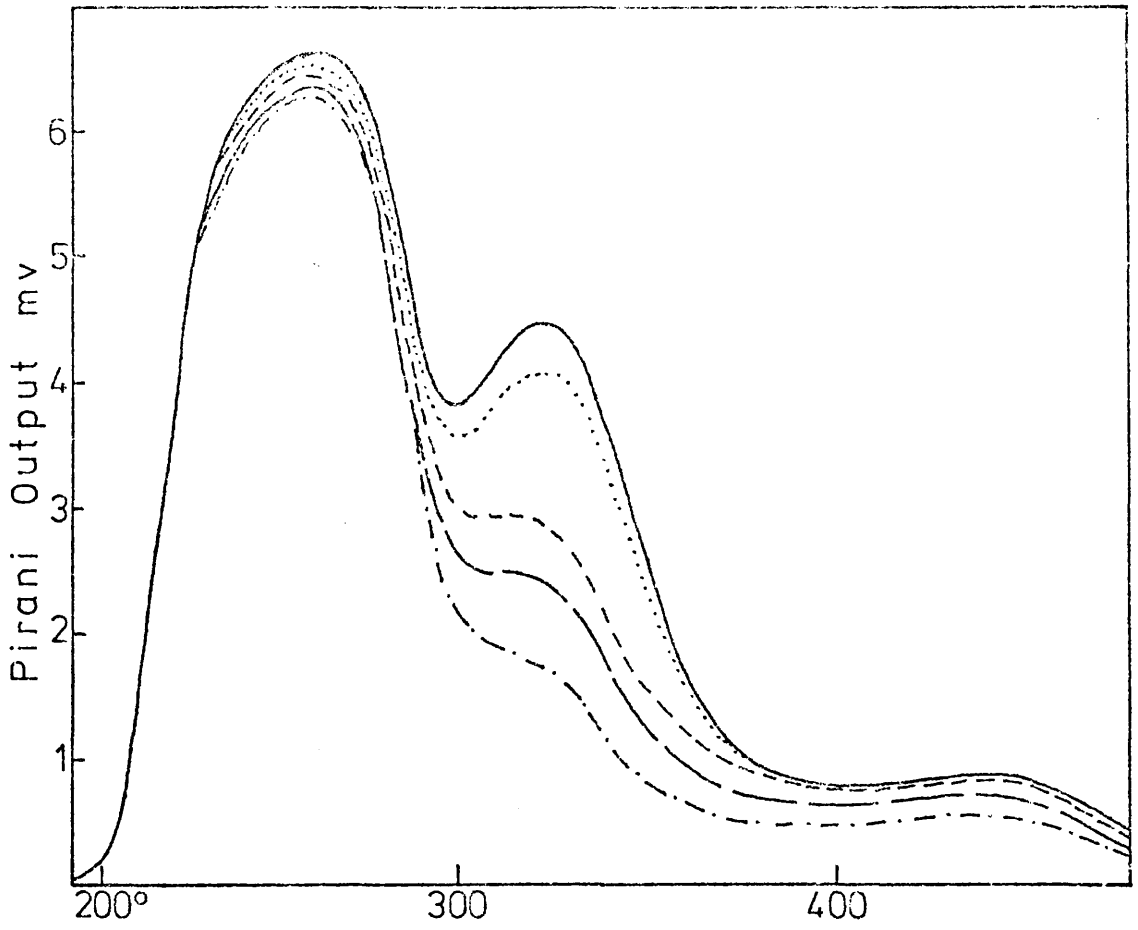


Figure (8.1). TVA trace for a 50 mg film sample of PVF (III). Heating rate 10°C/min, solvent methyl formate.
Key to traces p.35

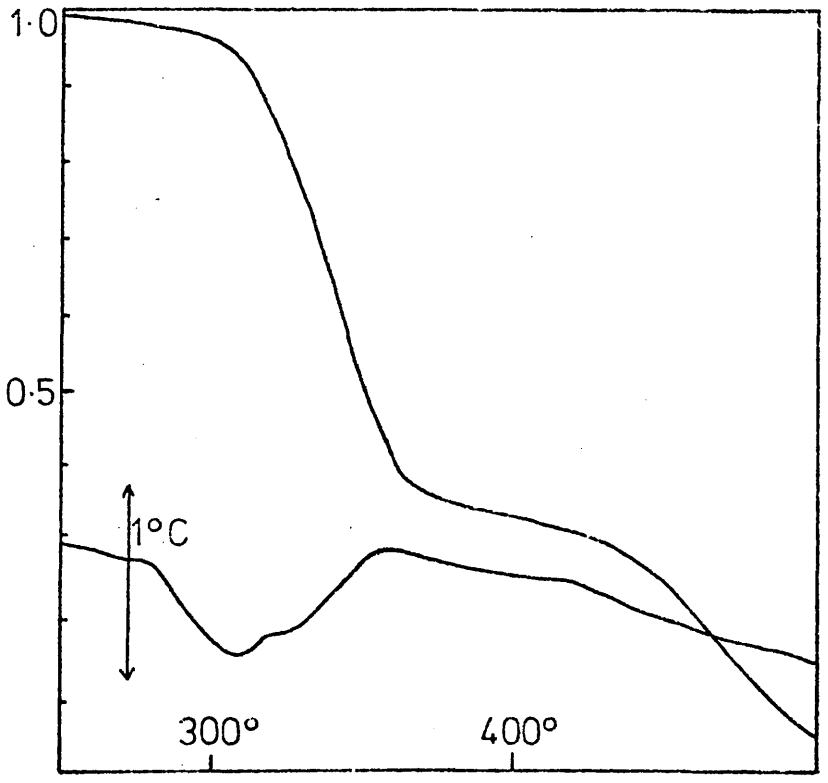


Figure (8.2). TG and DTA curves for 10 mg powder samples of PVF (III). Heating rate 10°C/min, under nitrogen.

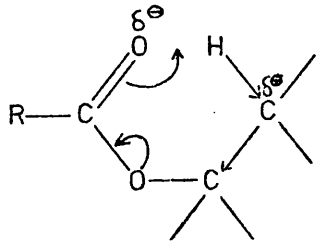
of PVF (III) using the Du Pont thermobalance. Figure (8.3) shows the weight loss at various times for degradation temperatures between 238° and 282°C. The activation energy, E, and the pre-exponential factor A, were determined by applying the Arrhenius equation to the logarithm of the initial rates (up to 10% weight loss) of figure (8.3). A graph was made of log (initial rate) vs (absolute temperature)$^{-1}$, and this is reproduced in figure (8.4). The best straight line and standard deviation of the gradient and the intercept were calculated by the least squares method. From the gradient and intercept,

$$E = 41.2 \pm 1.5 \text{ k.cals/mole}$$

$$\log_{10} A = 16.4 \pm 0.6$$

DISCUSSION.

The thermal decomposition of "model" ester compounds like ethyl and isopropyl formates has been investigated and discussed by Maccoll (18), who obtained values of 44.0 and 44.2 k.cals/mole for E, and 12.58 and 12.33 for $\log_{10}A$, for isopropyl formate; and 44.13 for E and 11.33 for $\log_{10}A$ for ethyl formate. The value of E determined for PVF is fairly close to those for these low molecular weight formates, although the value for the pre-exponential factor is considerably greater for the polymer. To account for the decomposition of these "model" esters Maccoll (18) proposed a unimolecular mechanism for olefin elimination, which has the transition state,



It may be that a similar mechanism is in operation in the degradation of PVF.

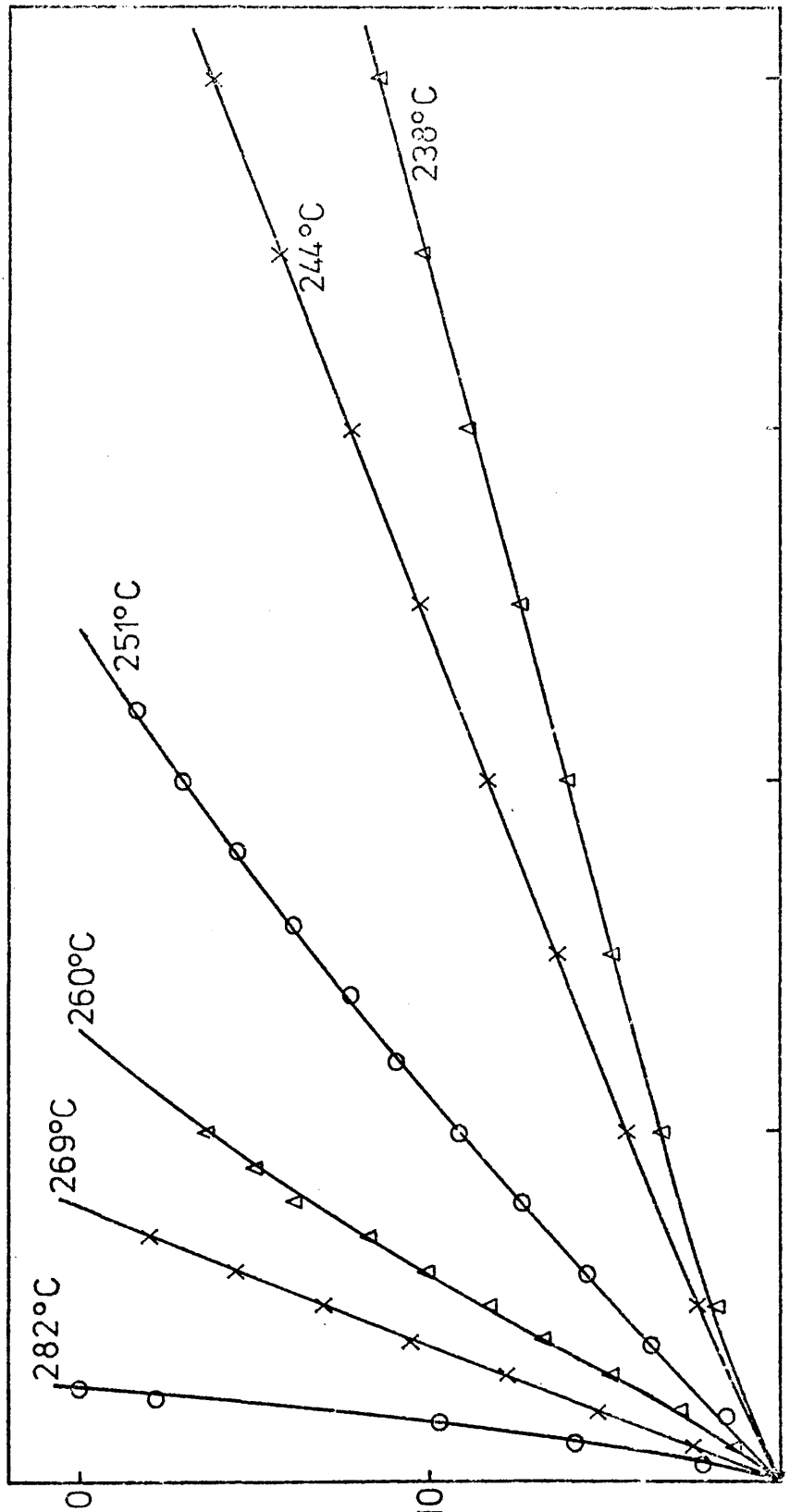


Figure (8.3). Isothermal weight loss curves for degradation of PVF (III), (10 mg powder samples), under nitrogen at temperatures between 238° and 282°C.

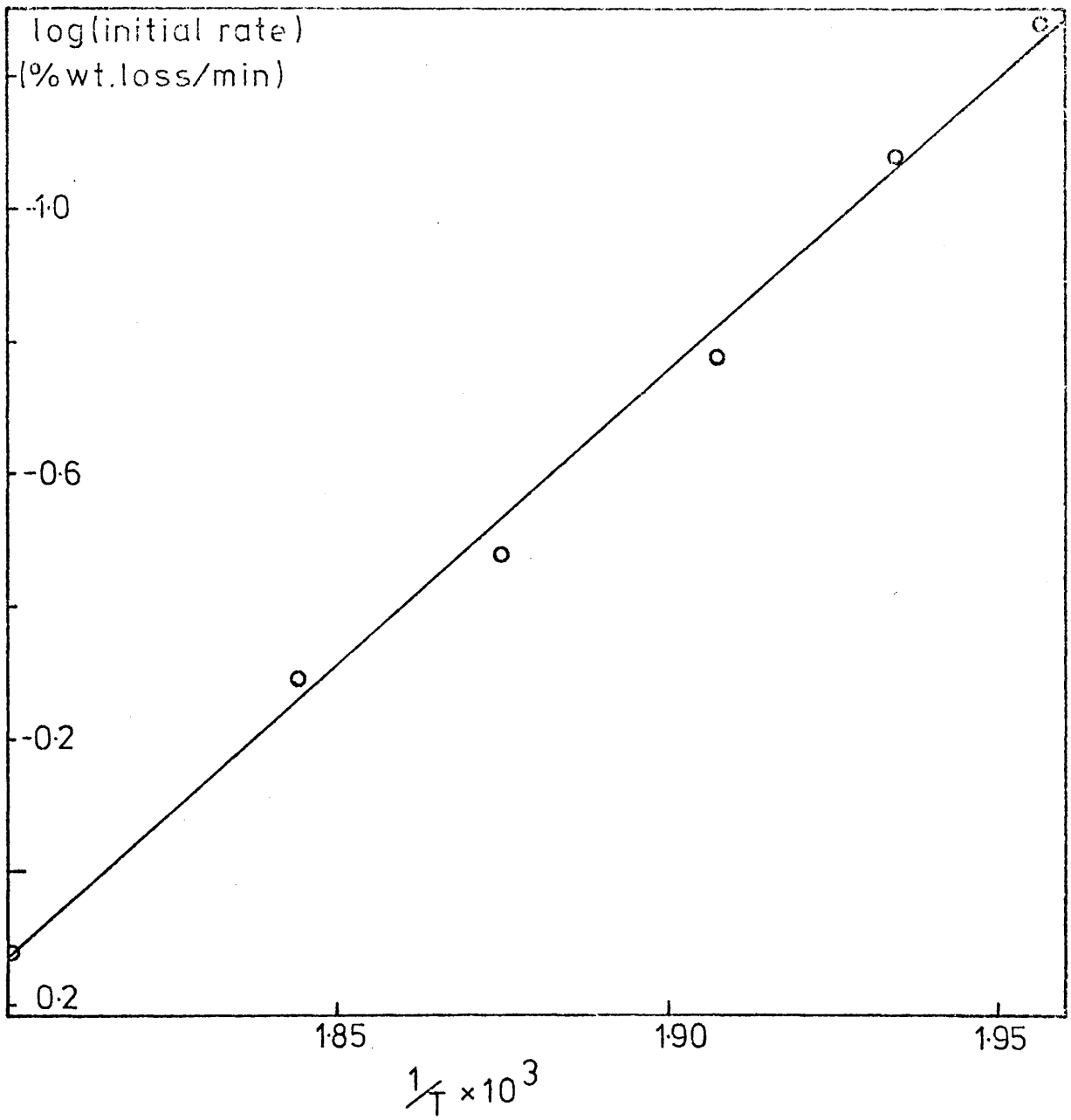


Figure (8.4). Graph of log (initial rate) vs $^{1}/T$ for isothermal degradations of PVF (III).

UV spectroscopic analysis reveals that the PVF residue is very similar to the PVA residue (36), and just as for PVA, this appears to suggest that initiation of deformylation is random in nature. Although it is possible that breakdown of formyl radicals is responsible for the formation of CO_2, CO and CH_4, it is more likely that these products arise from secondary decomposition of formic acid which undergoes more than 90% degradation at 450°C (82), and in fact can decarboxylate at temperatures as low as 160°C (83). Nelson and Engelder (82) found that formic acid was so sensitive to catalytic influence in its decomposition that it was considerably affected by the walls of the reaction tube, and this very sensitive decomposition of formic acid may be the cause of the different TVA behaviour for different sample forms of PVF. It was suggested (82) that the principal reaction route for formic acid decomposition is,

$$HCOOH \longrightarrow CO_2 + H_2 ,$$

with an extremely small amount (less than 1% below 350°C) of,

$$2HCOOH \longrightarrow CO_2 + H_2O + HCHO.$$

The two reactions,

$$HCOOH \longrightarrow CO + H_2O$$

$$HCHO \longrightarrow CO + H_2 ,$$

account for the 2% CO formed. While these reactions satisfactorily account for the production of CO_2 and CO and also for the large amount of material non-condensable at -196°C (viz. H_2), it is difficult to account for the formation of CH_4.

However, there seems to be a discrepancy between the TG and TVA results in that the former indicate a smooth one-stage loss of weight of formic acid, while the latter show evidence for a two-stage reaction. Also the TVA curve exhibits production of more non-condensable material at low temperatures instead of at high temperatures as might be expected

if formic acid decomposition were the only process responsible for its production. This suggests that the degradation of PVF may not be quite as straightforward as it initially appears.

THE DEGRADATION OF PVF-PMMA BLENDS.

In an effort to obtain information on the actual mechanism of deformylation, the degradation of PVF - PMMA blends was studied using TVA. TVA traces for equal weights of PVF and PMMA, degraded simultaneously as unmixed and mixed samples, were obtained, but interpretation was complicated by the relatively large PVF peak which obscured to some extent the peak for depolymerization of PMMA. In figure (8.5) are reproduced TVA traces for 1:5 by weight ratios of PVF (III) and PMMA R1, degraded simultaneously as unmixed and mixed samples.

For the "unmixed" trace, the complex peak and shoulder of PVF is clearly defined below 300°C, while the peak for MMA monomer production occurs above 300°C. In the "mixed" trace PVF deformylation results in a single peak without a shoulder, and there is no evidence of accelerated decomposition of PMMA. Indeed, the PMMA peak occurs at higher temperatures in the mixed system and there is also an increase in the production of non-condensables above 400°C. This stabliization and non-condensable production may result from the occurrence of anhydride structures in the PMMA chain, through interaction of formic acid with the methacrylate ester groups. Inspite of the delay in volatilization from PVF, there is no indication of accelerated MMA monomer production which suggests that radicals are not produced during deformylation. The delay in volatiles production from PVF (shown on the TVA trace) may be caused by the heterogeneity of the blend system, since it was shown previously that the pattern of PVF volatilisation is susceptible to sample form.

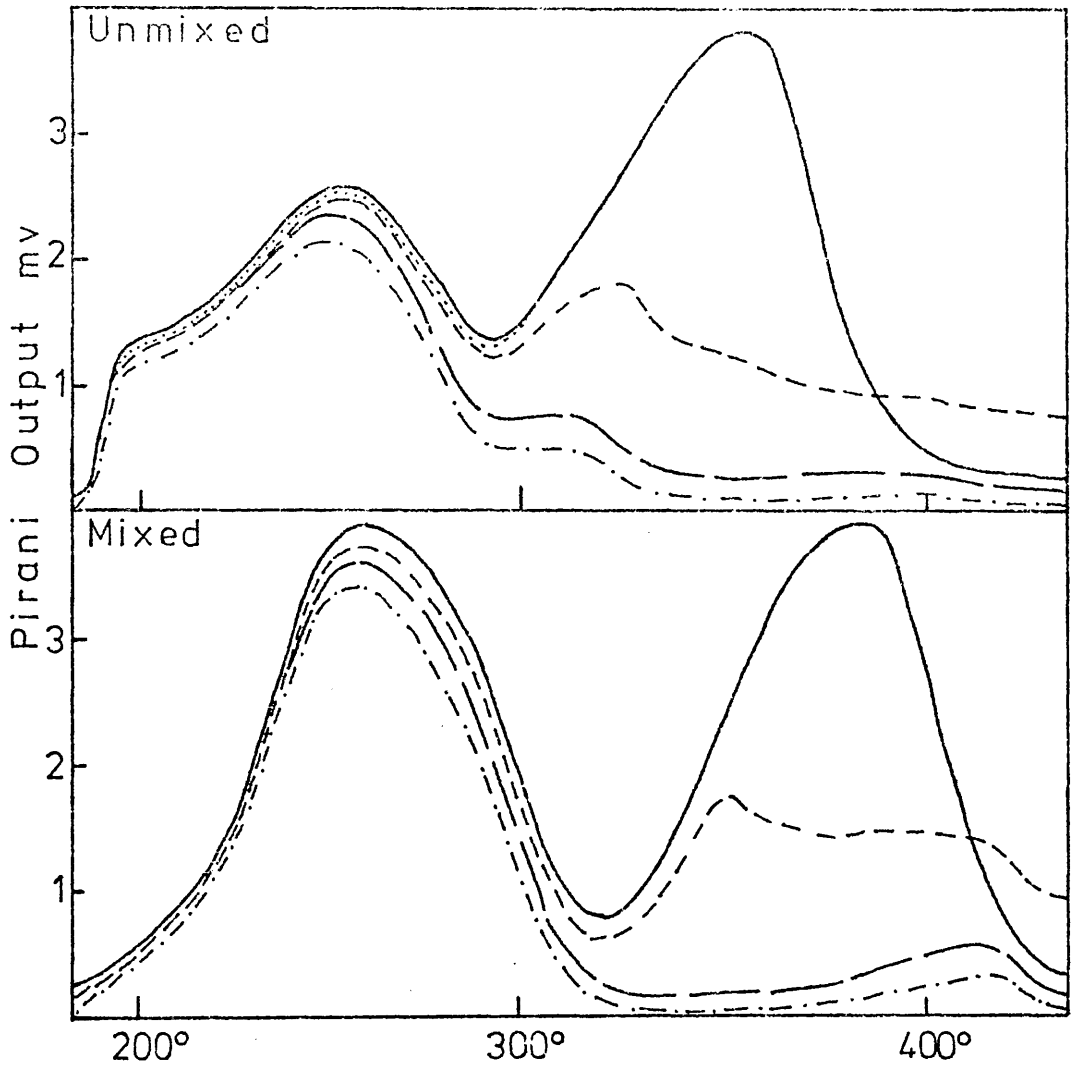


Figure (8.5). TVA curves for simultaneous degradation of PVF (III), 4 mg, and PMMA R1, 20 mg as unmixed and mixed film samples. Heating rate 10°C/min, solvent methyl formate.

THE DEGRADATION OF PVF-PVA BLENDS.

The degradation of these mixtures was investigated to assess the effect of formic acid on the deacetylation of PVA. Once again, TVA traces of the 1:1 by weight system were extremely difficult to interpret because of the relatively large PVF peak, and hence TVA traces for the 5:1 by weight PVA:PVF system were obtained, and these are reproduced in figures (8.6) and (8.7) for the unmixed and mixed samples respectively. In both systems, the peak with Tmax above 300°C is due to deacetylation of PVA, while that below 300°C is for PVF deformylation.

Apart from a small difference in the PVF volatilization pattern, which is probably a result of the previously discussed sample form effect, the overall behaviour of both systems is similar. The PVA peak is unaffected by degradation in the presence of PVF, and hence formic acid, unlike HCl, does not cause acceleration of PVA deacetylation.

SUMMARY.

The degradation of PVF has been briefly studied and the activation energy of the elimination reaction calculated. The mechanism of elimination has been considered, and the yield of formic acid obtained indicates that secondary decomposition of formic acid, to give highly volatile products, is occurring.

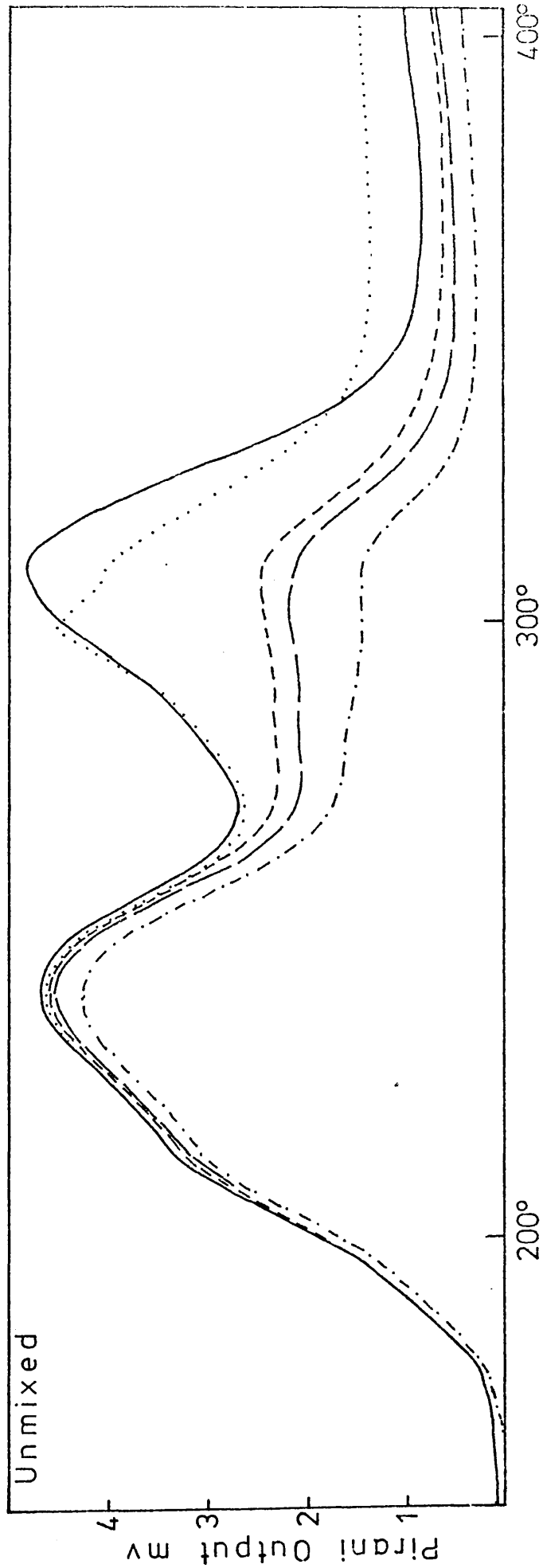


Figure (8.6). TVA trace for simultaneous degradation of PVF (III), 8 mg, and PVA (BDH), 40 mg, as unmixed film samples. Heating rate 5°C/min, solvent system methyl formate.

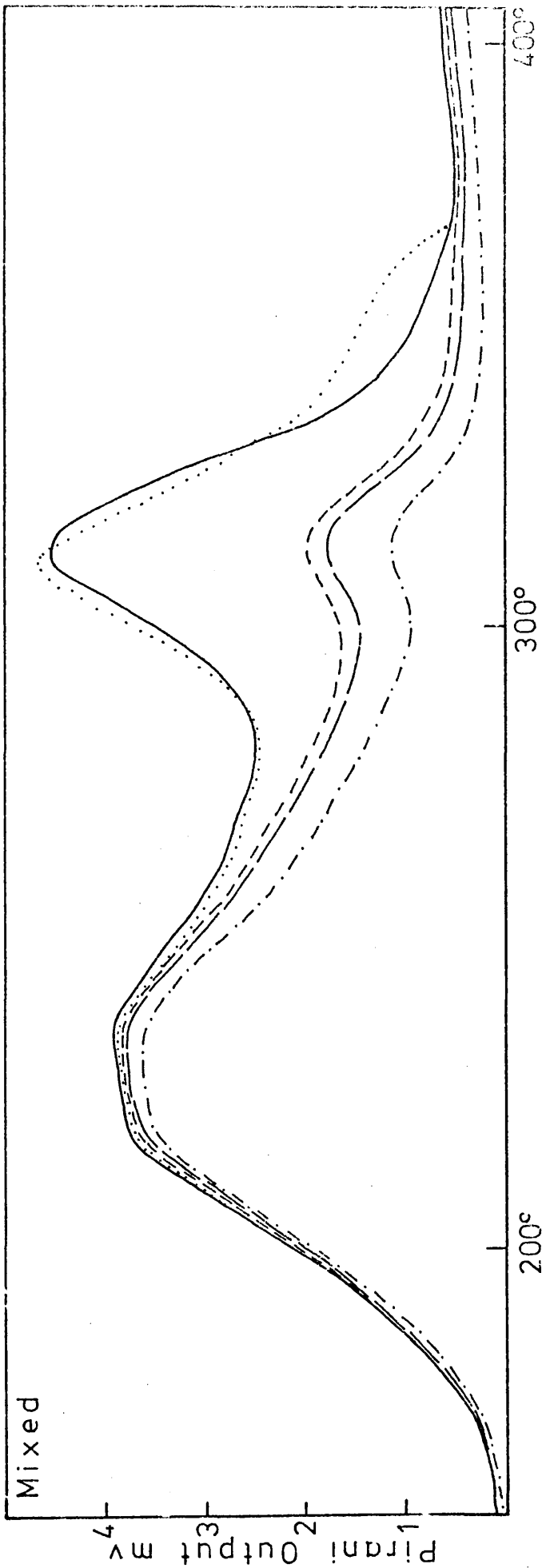


Figure (8.7). TVA trace for simultaneous degradation of PVF(III), 8 mg, and PVA (BDH), 40 mg, as mixed film samples. Heating rate 5°C/min, solvent system methyl formate.

CHAPTER NINE

THE DEGRADATION OF MISCELLANEOUS MIXED POLYMER SYSTEMS

INTRODUCTION

During the course of this work on the degradation of polymer blends and copolymers described in previous chapters, several mixed polymer systems were briefly examined, and some of these are described in this chapter.

POLYMERS USED

PMMA (SC) was prepared in bulk at 40°C using 0.05% AIBN as initiator. The number - average molecular weight was 383,000.

Poly (n-butyl methacrylate) (PBMA) samples were prepared by polymerization in bulk at 60°C, using AIBN as initiator. The number - average molecular weights were; PBMA 1, 684,000; PBMA 2, 815,000.

The preparation and histories of the other polymer samples have been described in previous chapters.

ALLOPRENE - PMMA BLENDS

Some of the experiments in this work were carried out by Mr. S. Crawley.

The degradation of both alloprene and PMMA has been discussed in previous chapters in some detail, and it might be expected that the degradation of alloprene - PMMA mixtures would show some features similar to those observed during degradation of PVC - PMMA blends.

THERMAL VOLATILIZATION ANALYSIS

TVA traces for equal weights of alloprene and PMMA (FR1) are shown in figure (9.1). The "unmixed" trace shows two peaks; the first with Tmax around 280°C is composed mostly of material non-

condensable at -100°C which is HCl from decomposition of alloprene: the second peak with Tmax around 360°C is MMA monomer from PMMA (limiting rate at -75°C). At the first peak there is a product evolved which is condensable at -100°C, and this is probably MMA monomer which indicates a certain degree of overlapping of HCl production and MMA monomer production (from chain end initiated depolymerization). For the "mixed" trace two peaks are evident, but the one at lower temperatures is broader and has a greater amount of material condensable at -100°C (MMA monomer); there is also a slight delay in the production of HCl, compared to the unmixed trace. The second peak occurs at higher temperatures in the blend and has a greater amount of material non - condensable at -196°C (around 400°C). Thus this system exhibits TVA behaviour (accelerated MMA production at lower temperatures and subsequent stabilisation of PMMA) which is similar to that observed in the PVC - PMMA blends (20).

TVA traces for the powder system are reproduced in figure (9.2). Production of an increased amount of MMA at lower temperatures is obtained in the mixed system, and there is a corresponding decrease in height for the PMMA peak which has a higher Tmax than in the "unmixed" trace and shows a very small amount of non - condensable production.

TVA traces for the 5:1 by weight ratio of PMMA: alloprene are shown in figure (9.3). The stabilisation of PMMA and production of non - condensables at higher temperatures are apparent in the mixed trace. At lower temperatures there is evidence for a slight delay in HCl production and accelerated MMA production, but the magnitude of both these effects is much less than in the 1:1 by weight ratio.

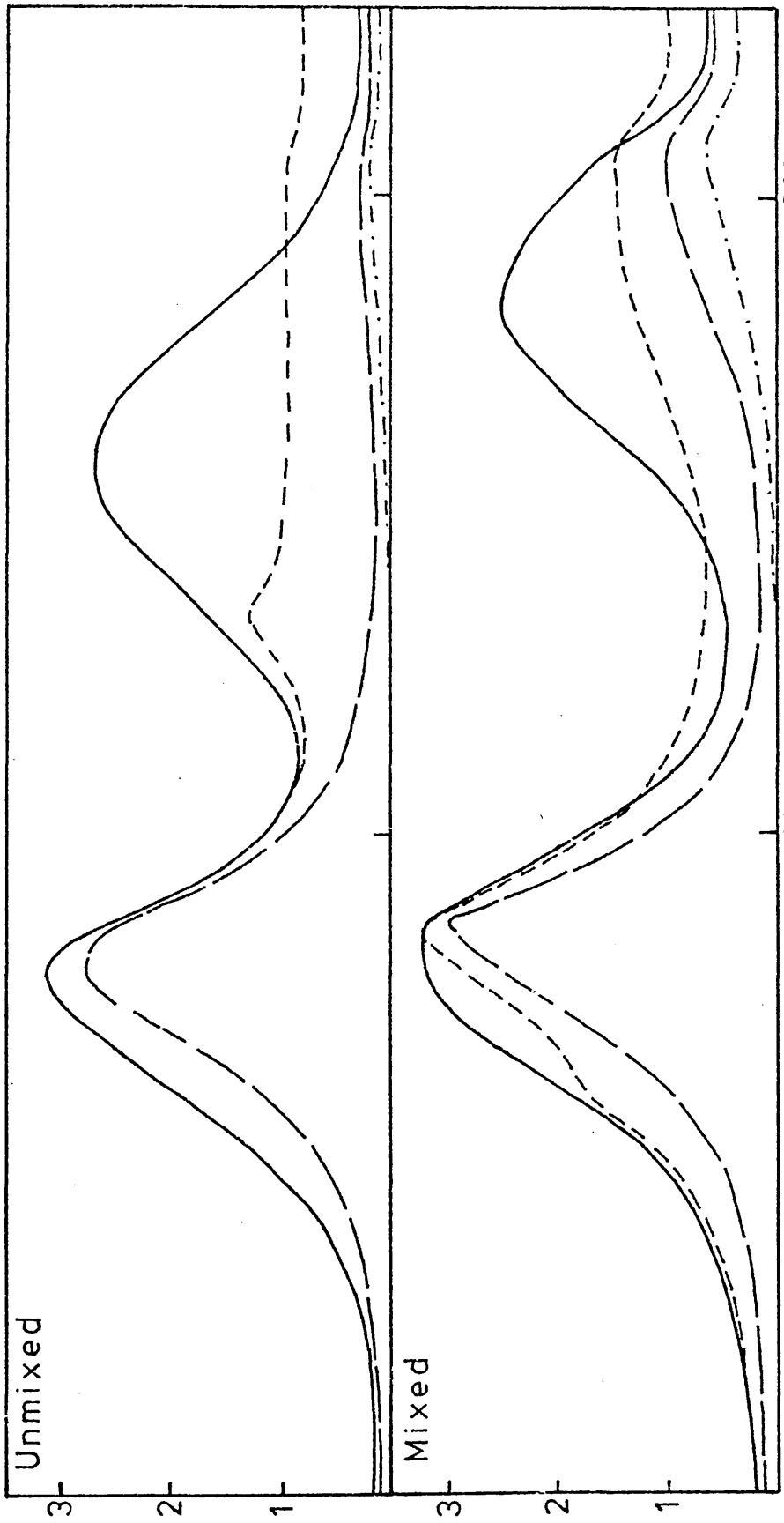


Figure (9.1). TVA curves for simultaneous degradation of PMMA (FR1) and alloprene, 30 mg of each, (a) unmixed, (b) mixed. Film samples, heating rate 5°C/min. Solvent methylene chloride. Key to traces page 35.

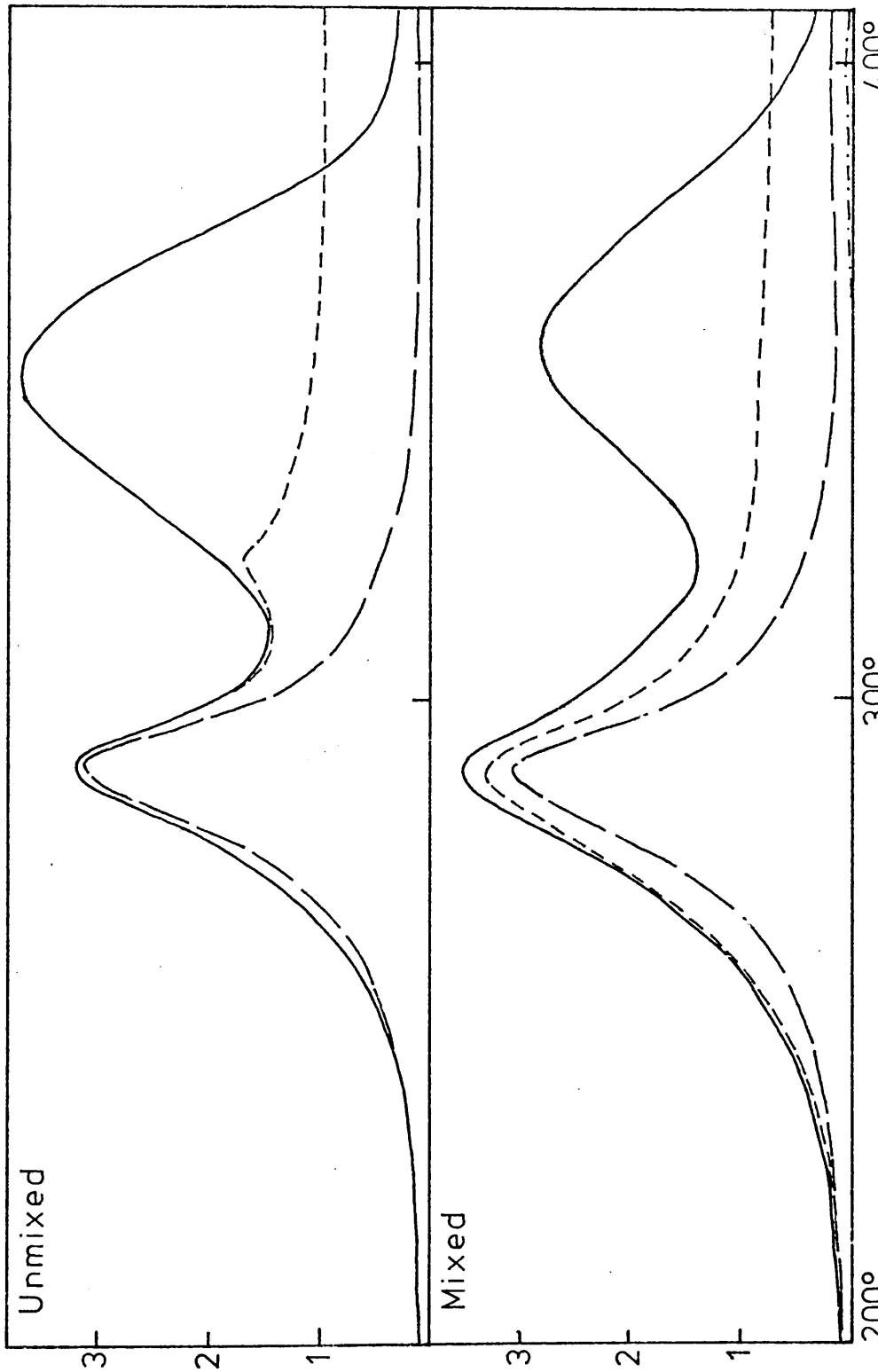


Figure (9.2). TVA curves for simultaneous degradation of PMMA (FR1) and alloprene in an unmixed and mixed condition. 30 mg of each polymer as powders, at a heating rate of 5°C/min.

The TVA evidence suggests that the degradation of PMMA is accelerated in blends with alloprene, and that there is a corresponding delay in HCl production. At higher temperatures there is stabilisation of PMMA depolymerization and production of a considerable amount of non - condensables.

Thermogravimetry

In figure (9.4) are reproduced TG curves for PMMA and alloprene. The curve for PMMA shows 100% weight loss for depolymerization monomer. The curve for alloprene exhibits a one - stage weight loss of 64% up to 350°C, which corresponds to dehydrochlorination. From 350°C to 500°C the weight loss is only 3%.

The "expected" TG curve for a 1:1 by weight mixture of these polymers was constructed by addition, and this can be compared with the observed curve in figure (9.4). The observed curve shows an accelerated rate of weight loss in the temperature region 200° - 380°C compared to the "expected" curve. Above 380°C the observed curve shows increased stability compared to the "expected" curve. Both these observations support the evidence obtained by TVA.

VOLATILES ANALYSIS

Infra-red spectra were obtained for the products of degradation (to 500°C) of a 1:1 by weight mixed film of PMMA and alloprene. Products identified were HCl, MMA monomer, CO_2 and methanol.

Mass spectra of products of degradation of mixed film and powder samples confirmed the presence of the above compounds, but also revealed the presence of a trace of methyl chloride. Figure (9.5) shows spectra for products non - condensable and condensable at -90°C. Signals at $^{M}/_{e}$ values of 100, 69 and 41 can be attributed to MMA and its fragments; peaks at 36 and 38 are due to $H^{35}Cl$ and

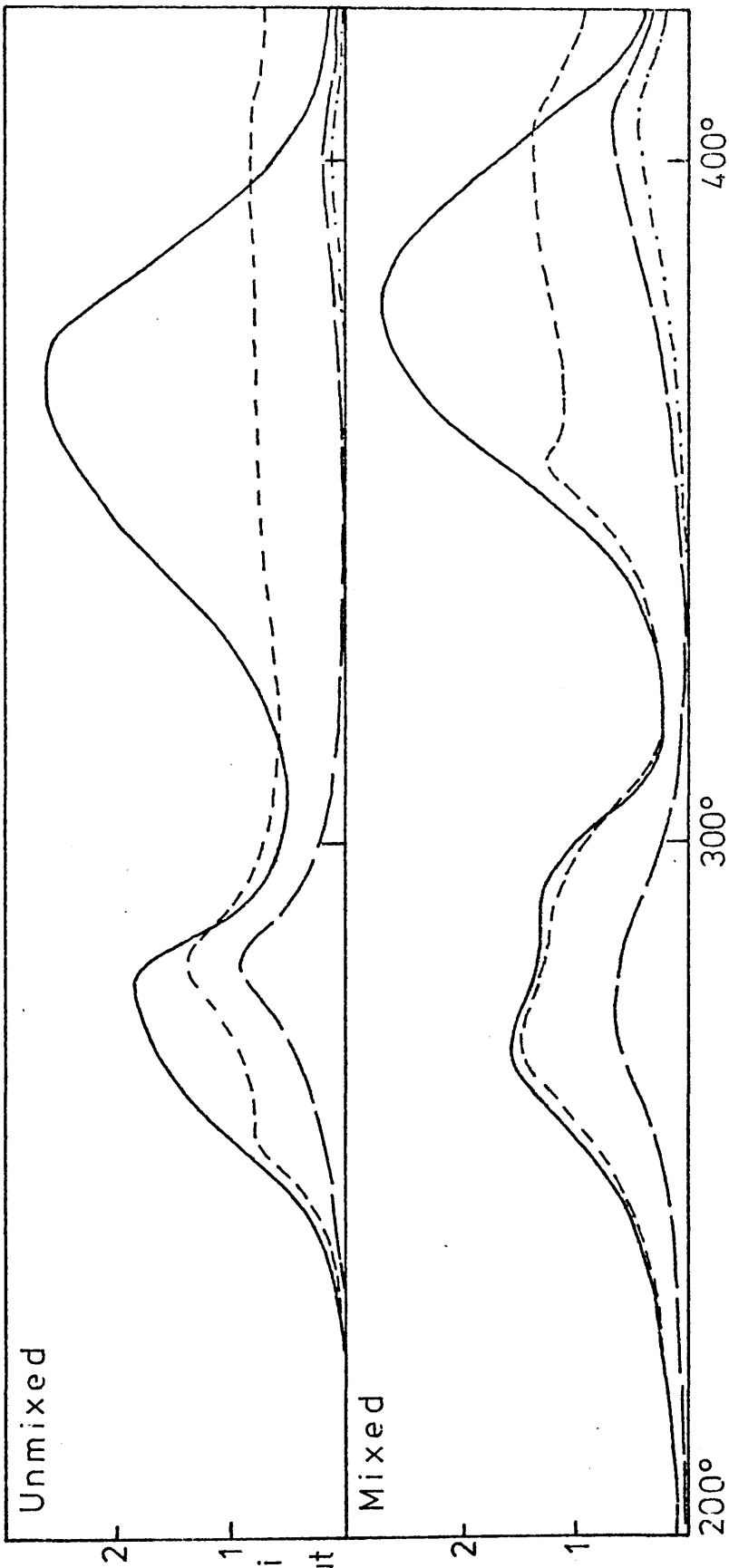


Figure (9.3). TVA traces for simultaneous degradation of PMMA (FR1), 30 mg, and alloprene, 6 mg, as unmixed and mixed films. Heating rate 5°C/min, solvent methylene chloride.

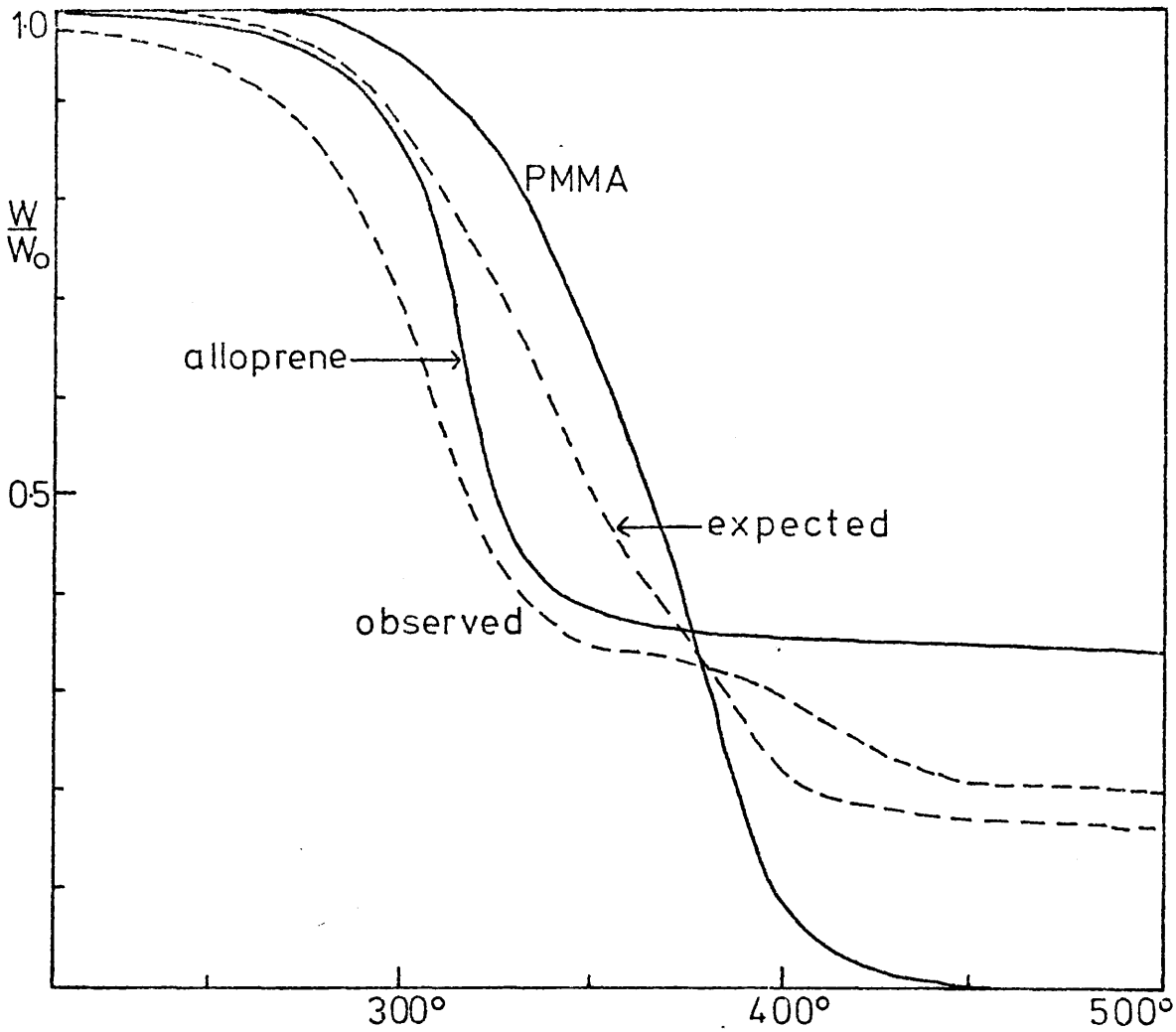


Figure (9.4). TG curves for alloprene and PMMA (SC), and for 1:1 by weight mixture of alloprene and PMMA (SC). Also included is the expected behaviour in the absence of interaction between the polymers. Powder samples (10 mg) degraded at $10^{\circ}C$/min under nitrogen.

$H^{37}Cl$ respectively. HCl is the principal product in the fraction non - condensable at -90°C, MMA being almost totally absent, while the reverse is the situation for the fraction condensable at -90°C. The small peaks at 50 and 52 ($^{M}/e$ values) in the non - condensable fraction are probably due to methyl chloride ($CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$), that at 44 to CO_2, while methanol can be identified by peaks at $^{M}/e$ values 31 and 32 in the condensable fraction.

In a manner analogous to the PVC - PMMA system, methyl chloride and methanol can result from interaction of HCl with the methacrylate ester groups, while CO_2 can be evolved by subsequent decomposition of the anhydride structures so formed.

DISCUSSION

It appears that the degradation of PMMA in the presence of alloprene is being accelerated considerably, and it is not unreasonable to draw comparisons between this system and the PVC - PMMA one. However, until more is known about the structure and degradation of alloprene itself, it is probably not valid to assume that the radical species involved in chain scission of the PMMA chains is a chlorine radical, although it is difficult to envisage any other species being responsible. This interaction does provide evidence for a radical - type mechanism for the degradation of alloprene. The other phenomenon of PMMA stabilisation probably results from interaction of HCl from degrading alloprene with the methacrylate ester groups, forming anhydride structures which inhibit depolymerization.

POLY (VINYLIDENE CHLORIDE) - PMMA BLENDS

TVA traces for simultaneous degradation of equal weights of PVDC and PMMA in an unmixed and mixed condition (as powders), are shown in figure (9.6). PVDC undergoes loss of HCl on degradation (67), as previously discussed in chapter four, and in the "unmixed"

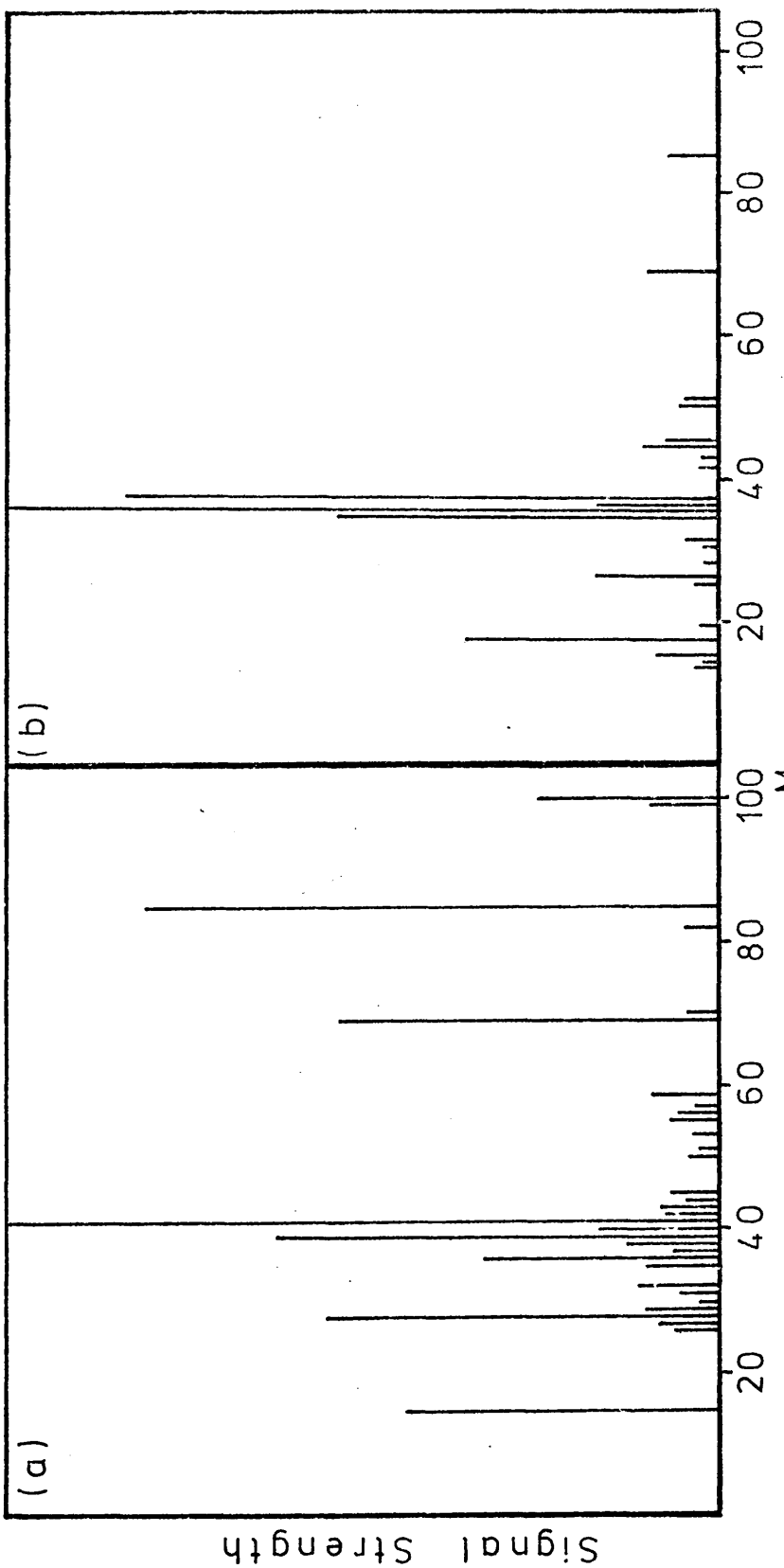


Figure (9.5). Mass spectra of products of degradation to 500°C of a PMMA (FR1) - alloprene mixture (equal weights of each polymer). Samples as powders, 100 mg total weight. (a) products condensed at -90°C, (b) products non - condensable at -90°C.

trace the small peak with Tmax around 230°C corresponds to dehydrochlorination of PVDC (HCl is non - condensable at -100°C). The larger peak above 300°C, with a limiting rate in the -75°C trace, corresponds to depolymerization of PMMA. The divergence of the -100°C trace from the 0°, -45° and -75°C traces occurs at about 265°C, indicating the commencement of production of some material condensable at -100°C, viz., MMA monomer.

The trace for the mixed system is very similar, except that production of MMA monomer occurs as low as 230°C, and is proceeding at a reasonable rate at the temperature at which it commences in the unmixed system. The PMMA peak itself is smaller and slightly broader in the mixed system; the former resulting from increased monomer production at lower temperatures and the latter from the very small amount of stabilisation of depolymerization by anhydride structures. That the latter effect is small can be seen from the fact that there is only a small amount of non - condensables production at higher temperatures.

Thus this system, in spite of being extremely heterogeneous (mixed powders), also indicates acceleration of PMMA depolymerization, presumably by a radical species like a chlorine atom which is an intermediate in the proposed radical dehydrochlorination of PVDC (67). The other interaction associated with this type of blend, viz, HCl on the methacrylate ester, only occurs to a very small extent.

BLENDS OF POLY (N-BUTYL METHACRYLATE) WITH PVC AND PVA

The degradation of poly (n-butyl methacrylate) (PBMA) has been investigated under isothermal conditions by Grassie and MacCallum (84). These workers found that in addition to monomer, butene is a minor product of degradation, due to an ester decomposition reaction in which methacrylic acid units are formed in the chain. These latter units can subsequently decompose. Ester decomposition occurs to a

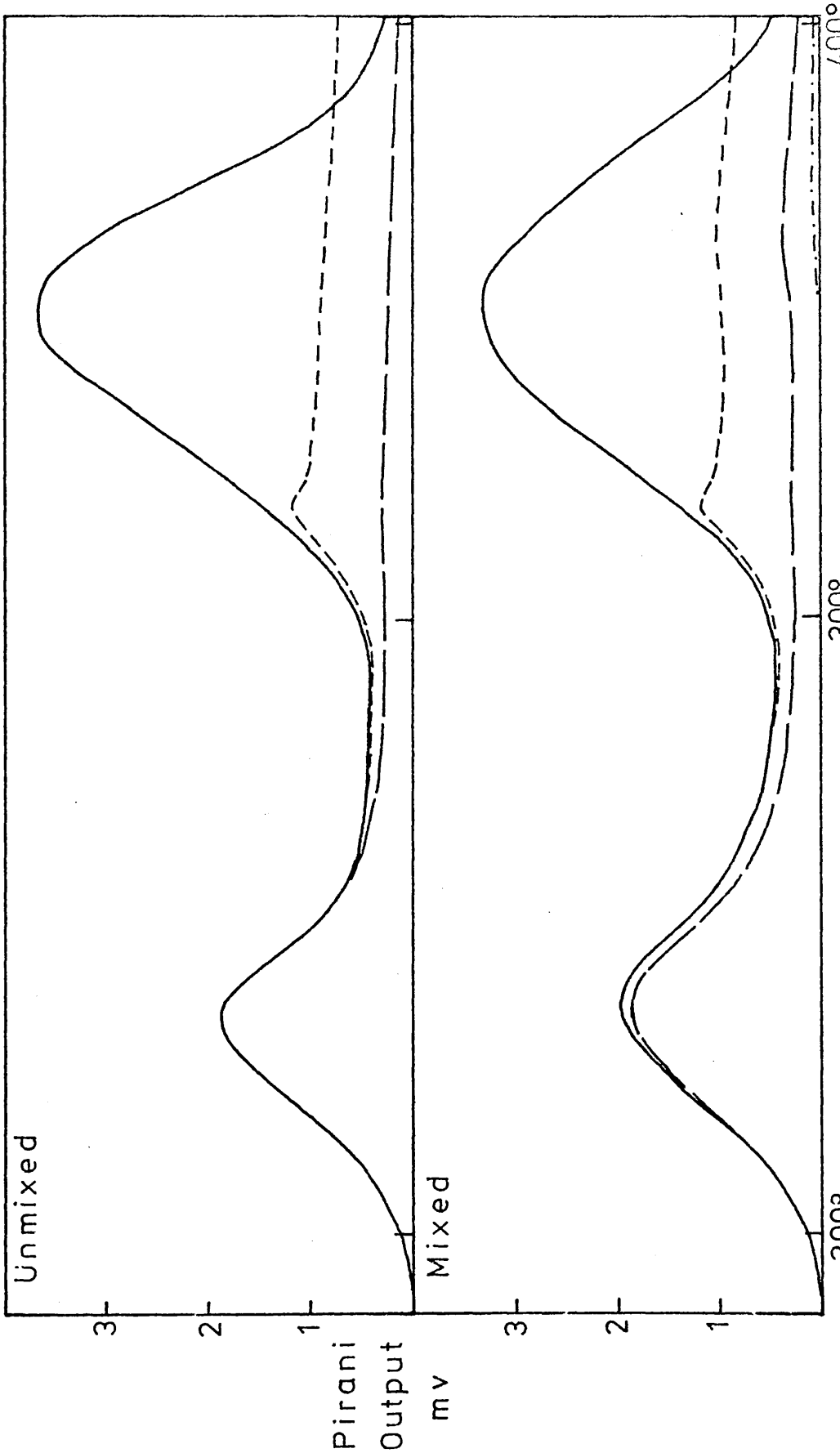


Figure (9.6). TVA curves for simultaneous degradation of PMMA (FR1) and PVDC (30 mg of each) in an unmixed and mixed condition. Powder samples at a heating rate of 5°C/min.

greater or lesser extent in all the polymethacrylates except the methyl exter (1), and in a few cases such as the t - butyl ester it occurs almost to the complete exclusion of depolymerization (11).

The TVA curve for PBMA, shown in figure (9.7), illustrates the breakdown of this material under programmed heating conditions. The rather involatile monomer gives the limiting rate effect observed in the -45°C trace. Butene production is seen from the -75°/-100°C traces to commence at about 270°C. The distinctive small peak in the -196°C trace results from the decomposition of the small amount of poly (methacrylic acid) type structures. These observations are in agreement with previous studies of the TVA behaviour of PBMA (77).

TVA traces for the 1:1 PVC - PBMA system are shown in figure (9.8), where, because of the complex nature of the traces, only those for the 0°C and -100°C trap temperatures are shown. For both systems, the peaks for the -100°C traces around 330°C are due to HCl volatilization, while the 0°C trace is due to production of BMA monomer (and HCl). It can be seen that there is a considerable increase in the size of the 0°C peak around 350°C in the mixed system. Since the amount of HCl evolved in both systems is approximately the same, this "extra" volatilization must be caused by BMA monomer. This phenomenon thus results in a substantial decrease in the amount of monomer produced at higher temperatures in the mixed system. About 400°C in the mixed trace there is increased production of material non - condensable at -100°C (and at -196°C, although it is not shown in the figure). This probably results from decomposition of polymethacrylic acid structures produced by interaction of HCl with the PBMA ester groups. Thus in the mixed system, these acid structures are produced by two routes; viz, ester decomposition and by the HCl interaction described.

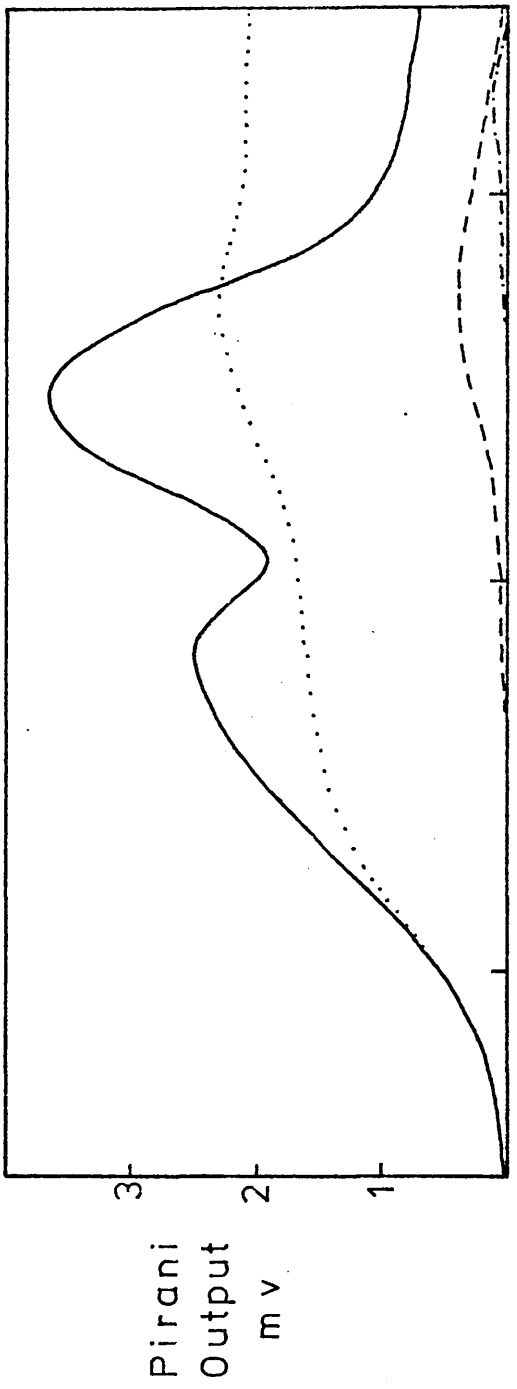


Figure (9.7). TVA trace for PBMA 1 as a 50 mg film. Heating rate $10^{o}C/min$; solvent benzene.

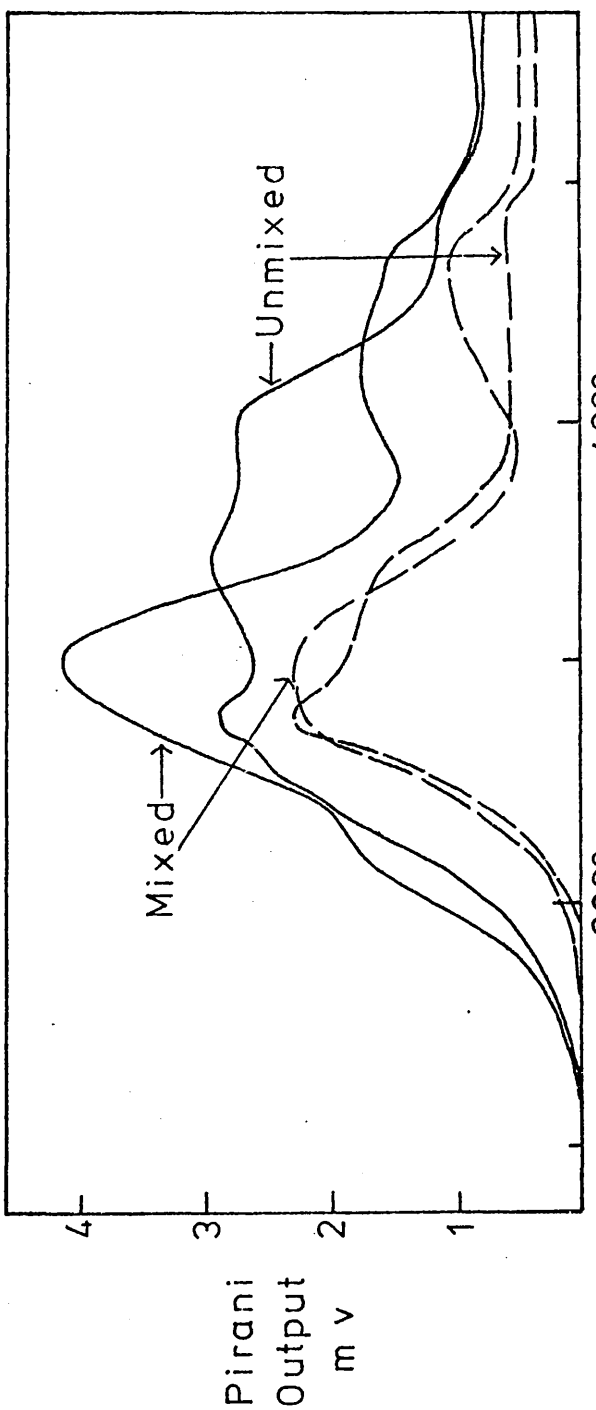


Figure (9.8). TVA curves for simultaneous degradation of PBMA 2 and PVC Breon 113, 25 mg of each, in an unmixed and mixed condition. Film samples, solvent cyclohexanone. Heating rate 10^{0}C/min, only the 0^{0}C and the -100^{0}C traces are shown.

A similar situation is observed for the PVA - PBMA system as can be seen in figure (9.9). In the "unmixed" trace, production of monomer begins about 200°C, while deacetylation begins about 280°C and reaches a maximum around 310°C (deacetylation can be followed by the displacement of the -196°C trace from the baseline, since this corresponds to the volatilization of the non - condensable products from acetic acid decomposition). Above 325°C, evolution of monomer and butene occur concurrently with the commencement of volatilization from breakdown of the PVA carbonaceous residue.

In the mixed trace deacetylation is virtually unaffected, but there is a greater amount of monomer evolved during the early stages of degradation (shown by an increase in the height of the peak with Tmax around 310°C). As a consequence of this latter effect there is a corresponding decrease in monomer production around 350°C. Above 400°C, there is a small increase in the amount of non - condensables produced compared to the unmixed system.

Thus it appears that the behaviour of PVA with PBMA is similar to that of PVC with PBMA and that both systems are analogous to the PVC - PMMA system.

BLENDS OF POLYACRYLONITRILE WITH PVA

This system was studied in conjunction with Mr. D. McDonald for comparison with the degradation of (vinyl acetate) - acrylonitrile copolymers. TVA curves for the 5:1 by weight ratio PAN : PVA system are shown in figure (9.10) for the samples as powders. The unmixed trace shows the sharp PAN volatilization peak around 290°C, at lower temperatures than the deacetylation peak for PVA. The mixed trace is extremely similar although the peak height for deacetylation is slightly smaller than in the unmixed trace. These effects were observed in TVA traces for several different ratios of the polymers.

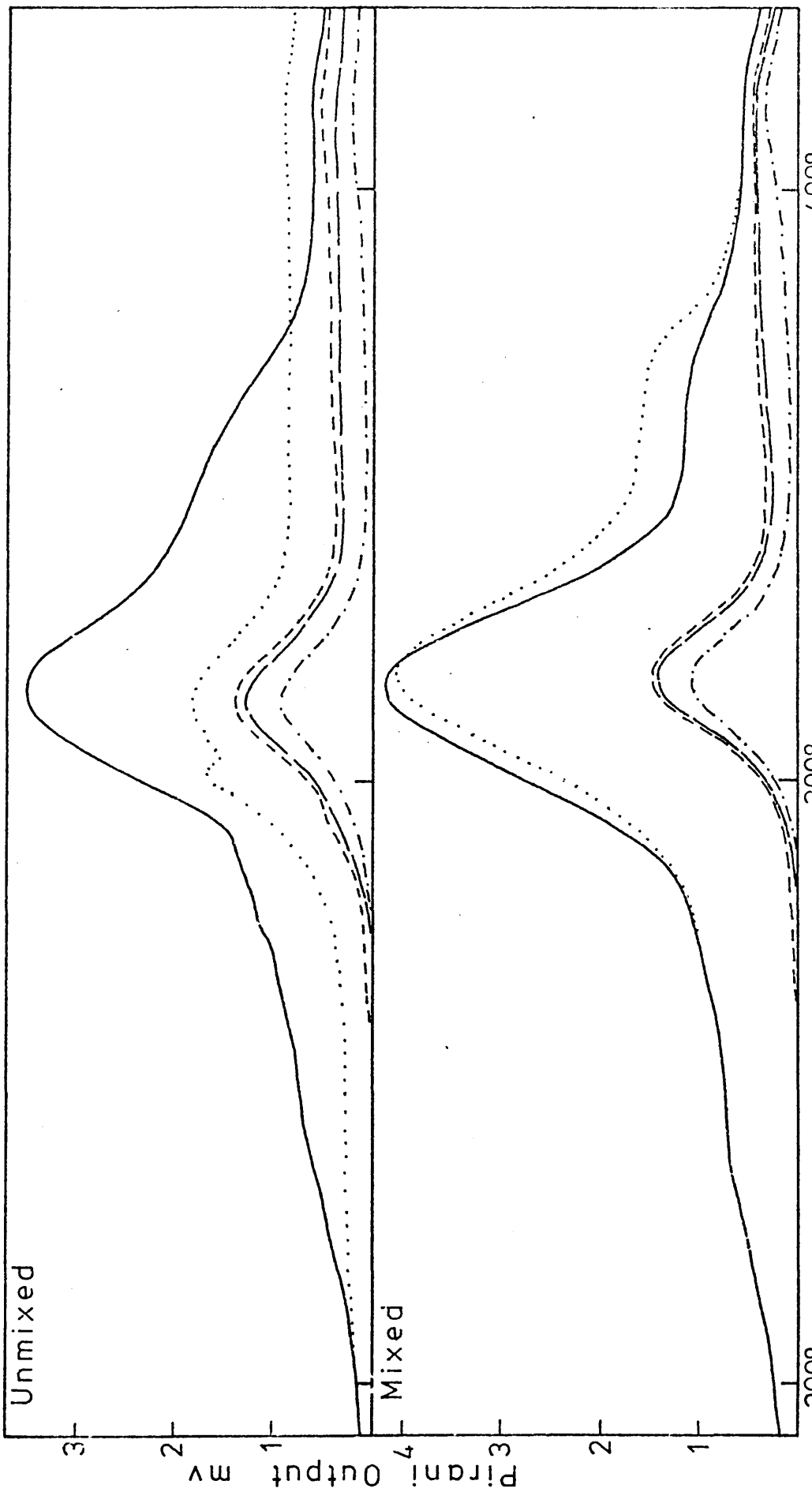


Figure (9.9). TVA curves for simultaneous degradation of PBMA 1 and PVA (BDH), 30 mg of each in an unmixed and mixed condition. Film samples, heating rate 5°C/min. Solvent benzene.

DTA investigations confirmed that there is little or no interaction between the polymers during degradation. The exotherm for PAN and the endotherm for PVA occur at the same temperature for the mixture as for the homopolymers alone. Also the values of the heat changes for both polymers in the blends were consistent with those for equivalent quantities of the respective homopolymers.

Infra - red spectroscopic analysis revealed that the products of degradation of the blends were those expected from degradation of the homopolymers alone. Thus apart from the small reduction in peak height for deacetylation (in the TVA trace of the blend) there are no apparent interactions between the polymers during degradation. An explanation for this decrease in the PVA peak in the TVA trace may be connected with the phenomenon that acetic acid and ammonia react to form ammonium acetate (72) as observed previously in the VA-AN copolymer system described in chapter six. It is possible that this reaction can occur at the reaction zone in the mixed sample, "removing" acetic acid and hence reducing the amount of material volatile at the various trap temperatures.

SUMMARY

It has been shown that alloprene and PVDC, when degraded as blends with PMMA, give rise to interactions similar to those observed in the PVC - PMMA system. Similarly, PVA and PVC, when degraded as mixtures with PBMA, cause initial accelerated depolymerization of PBMA to monomer, and subsequent stabilization of PBMA, by the formation of anhydride structures in the chain. PVA and PAN, when degraded as blends, apparently undergo their separate decompositions without any significant interactions.

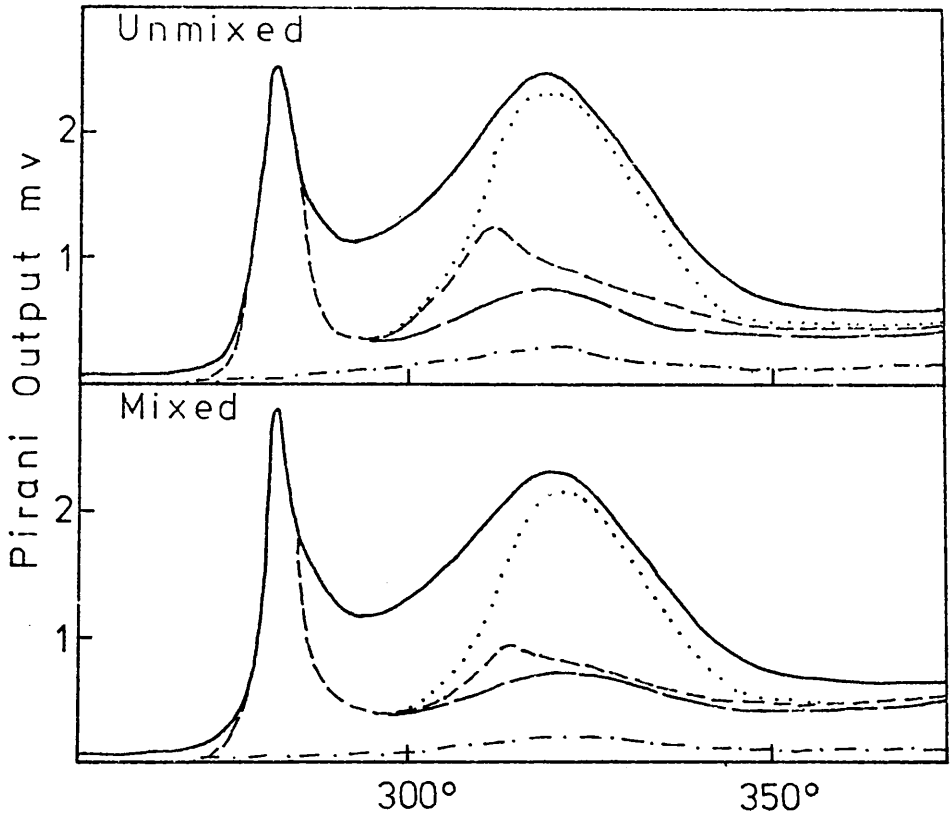


Figure (9.10). TVA curves for simultaneous degradation of PAN, 84 mg, and PVA (BDH), 16 mg, as unmixed and mixed powder samples. Heating rate 5°C/min.

CHAPTER TEN

POLYMER DEGRADATION IN THE PRESENCE OF SILVER ACETATE

The thermal degradation of silver acetate is similar in many respects to that of PVA, and for comparison with the degradation of blends incorporating PVA, the effect of heating polymers in the presence of silver acetate has been investigated.

INTRODUCTION.

Very little has been published about the mechanism of decomposition of metal acetates, (especially silver acetate), although Bernard and Busnot (85) have studied the thermal breakdown of a number using TG and DTA. These workers found that strontium and calcium acetates decomposed to the oxides at temperatures between 350° and 460°C via different varieties of acetate anhydrides and the carbonate, while magnesium decomposed to the oxide via a basic salt intermediate. Similar observations were made for zinc, cadmium, mercury, manganese, cobalt, nickel and copper, but no mechanism of reaction or product evolution was discussed to any great extent.

Investigations of the decomposition of silver, nickel, calcium and strontium acetates by TVA (32) has shown that there are considerable differences in the temperatures of degradation and that some give simple, single peak TVA traces, while others show more complex volatilization behaviour. There were also major differences in the types of product evolved; Ni-Ac gave products which were totally non-condensable at -100°C, whereas Ag-Ac gave a substantial proportion of products which were fully condensed at -75°C.

An investigation (86) of the decomposition of more than a dozen metal acetates, by TVA and infra-red spectroscopy, revealed that the

major degradation products are acetic acid, acetone, carbon dioxide and ketene, besides products which are non-condensable at liquid nitrogen temperatures. It was observed that some acetates evolved acetone, but not acetic acid, others gave acetic acid but not acetone, and yet others evolved both compounds. Thus, apart from acetone, the volatile degradation products are similar to those obtained from PVA decomposition and AgAc is in the category of metal acetates which does not give acetone as a degradation product.

Bell and Reed (87) using isotopic tracer techniques, studied the pyrolysis of barium acetate and formate mixtures and produced the following reaction scheme to explain the formation of acetone and acetaldehyde :-

Initiation	CH_3CO_2ba	$\longrightarrow CH_3^{\cdot} + {\cdot}CO_2ba$
Aldehyde formation	$CH_3^{\cdot} + HCO_2ba$	$\longrightarrow CH_3CHO + {\cdot}Oba$
Acetone "	$CH_3^{\cdot} + CH_3CO_2ba$	$\longrightarrow CH_3COCH_3 + {\cdot}Oba$
Propagation	$CH_3CO_2ba + {\cdot}Oba$	$\longrightarrow CH_3^{\cdot} + ba_2CO_3$
Termination	$2\,CH_3^{\cdot}$	$\longrightarrow C_2H_6 + CH_2^{\cdot} + CH_4$
	$2{\cdot}Oba$	$\longrightarrow (Oba)_2$
	${\cdot}CO_2ba + {\cdot}Oba$	$\longrightarrow ba_2CO_3$

(ba = ½ Ba)

Although this reaction scheme is not strictly applicable to the acetate system alone, nor to the silver acetate system which does not evolve acetone on degradation, it does serve to illustrate some of the many possible reaction pathways which can occur during decomposition of these metal acetates.

In this chapter the degradation of PMMA as a mixture with AgAc, will be considered in some detail and the decomposition of several

other polymers, including PVA, PBMA, PAN, PS, PVC, PAMS and Alloprene, will be briefly discussed.

EXPERIMENTAL

The AgAc used in this work was a BDH Ltd. laboratory reagent sample. PMMA FR1 (Mn 1,600,000) was prepared by D. Neil in bulk at 60°C using AIBN as initiator. PAMS was prepared at low temperature by anionic polymerization, in the Centre de la Recherche sur les Macromolecules in Strasbourg (28). The preparation and history of the other polymer samples have been given in previous chapters.

THE DEGRADATION OF SILVER ACETATE

The TVA behaviour of AgAc is reproduced in figure (10.1) and shows a sharp peak commencing at 215°C, with a Tmax value of 256°C. The 0° and -45°C traces are coincident and there are several other products, some of which are non-condensable at -196°C, shown by the lack of coincidence of the -75°, -100° and -196°C traces. Thus the peak for AgAc is similar to the peak obtained for deacetylation of PVA, although the latter is slightly broader, commences about 270°C, and has a Tmax at 328°C for a degradation rate of 5°C/min. The residue of the sample at 500°C, which was grey in colour before degradation, consisted mostly of a film of metallic silver, while the cold ring fraction was brown and white in colour.

The TG and DTA traces are shown in figure (10.2). The former illustrates that loss of weight commences just above 200°C and stabilises after 32% weight loss at 270°C. This region of weight loss corresponds to the area of volatilisation in the TVA curve. There is a very slow loss of weight between 270° and 500°C, at which point the total weight loss is 35.3%. The acetate content of AgAc accounts for 35.4% of the weight, and so it may be this species which

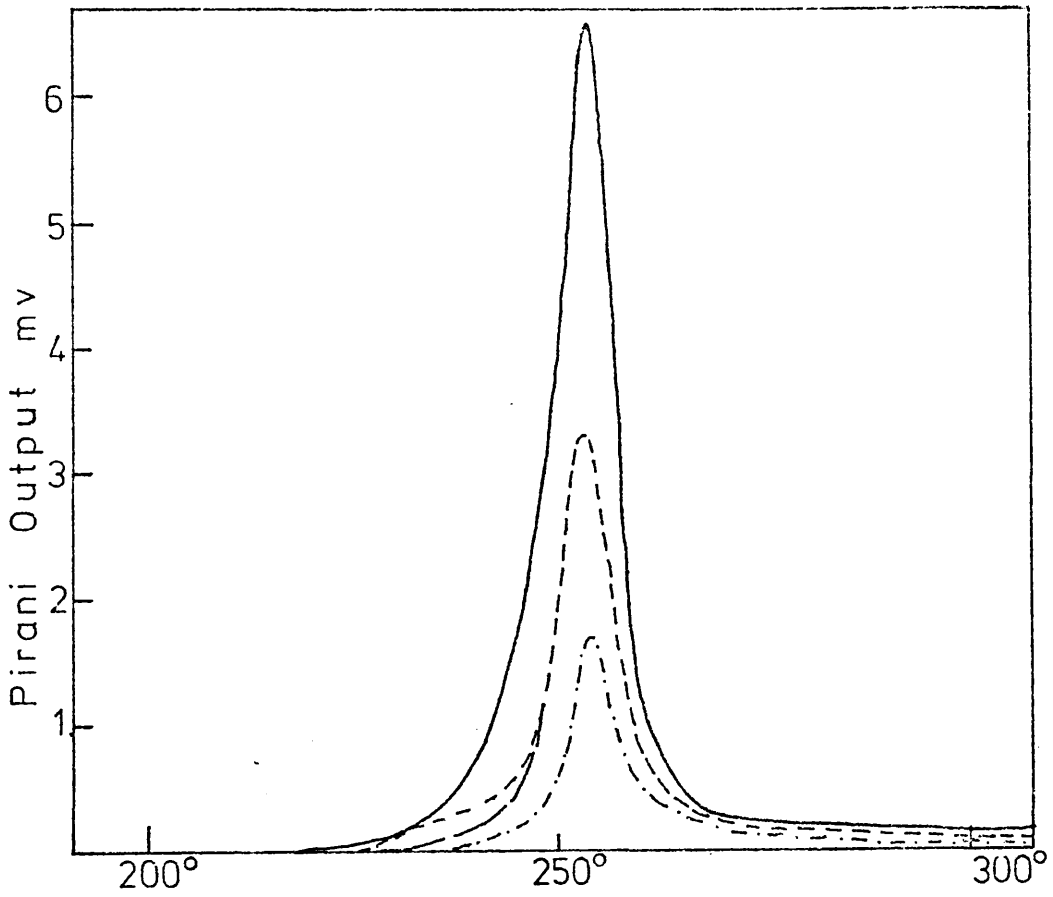


Figure (10.1). TVA trace for 50 mg powder sample of AgAc. Heating rate 5°C/min. Key to traces as on p.35.

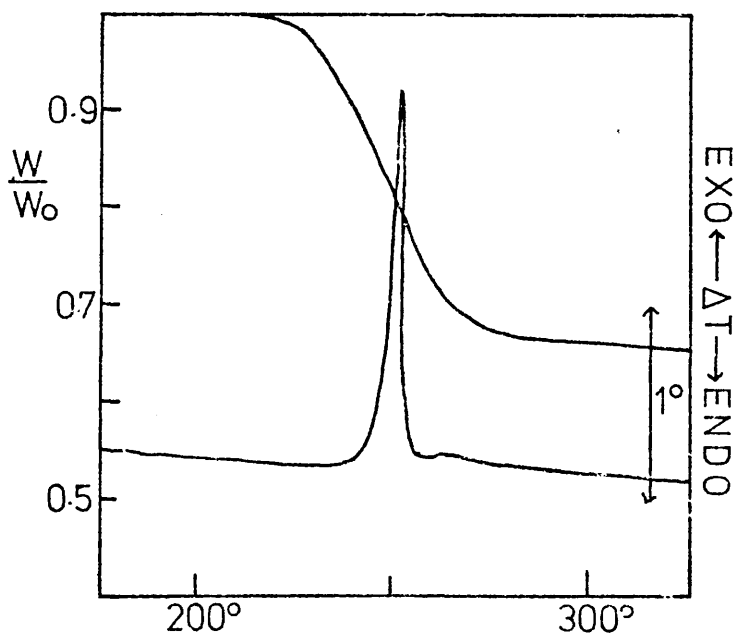


Figure (10.2). TG curve for 50 mg AgAc under vacuum at 5°C/min and DTA of 10 mg AgAc under N_2 at 5°C/min.

is somehow being lost. The DTA trace shows that the region of weight loss is accompanied by an exotherm of approximately 2°C, with a Tmax at 254°C.

Infra-red spectroscopic analysis of the volatile degradation products revealed acetic acid, carbon dioxide, ketene and carbon monoxide, but neither acetone nor methane were detected. Quantitative estimation of acetic acid by titration with $^{N}/_{100}$ NaOH using phenolphthalein as indicator, revealed that one mole of AgAc yielded 0.61 moles of acetic acid on degradation at 5°C/min to 500°C.

THE DEGRADATION OF AgAc - PMMA BLENDS.

THERMAL VOLATILIZATION ANALYSIS.

The TVA trace for AgAc has already been described, while that for PMMA FR1 is shown in figure (10.3) and is typical for a high molecular weight sample of PMMA; viz, a broad peak with Tmax 357°C for depolymerization initiated by random scission, with a very small shoulder below 300°C due to depolymerization initiated at chain ends.

The TVA traces for simultaneous degradation of equal weights of PMMA and AgAc, as unmixed and mixed powder samples, are shown in figure (10.4). The trace for the unmixed samples shows two distinct volatilization peaks for AgAc and PMMA; the former being the sharp one at lower temperatures, while the latter is broad, with a limiting rate at -75°C, and occurs at higher temperatures. The trace for the mixed system shows that production of volatile material at lower temperatures is considerably increased and that the temperature of initiation is below 200°C compared to 215°C for the unmixed system.

That this early volatilization is associated with MMA monomer is shown by the behaviour of the -75°C trace which exhibits a limiting rate early in the decomposition, and by the fact that the PMMA peak

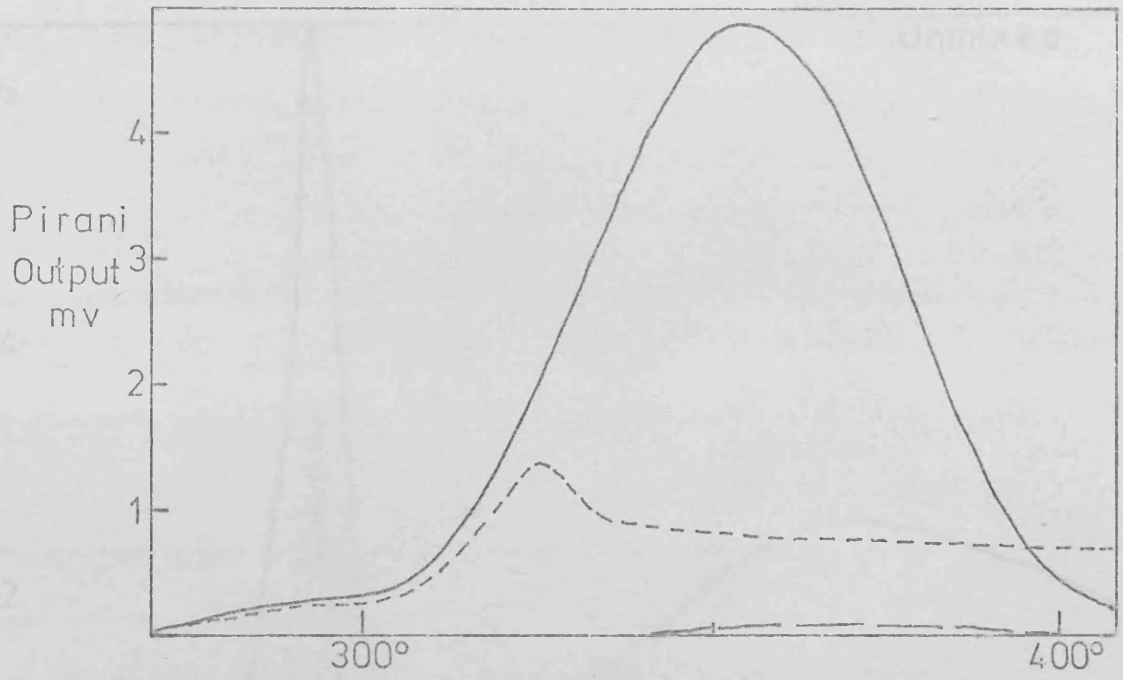


Figure (10.3). TVA trace for 50 mg PMMA FR1 as a powder sample at a heating rate of $5^{o}C$/min.

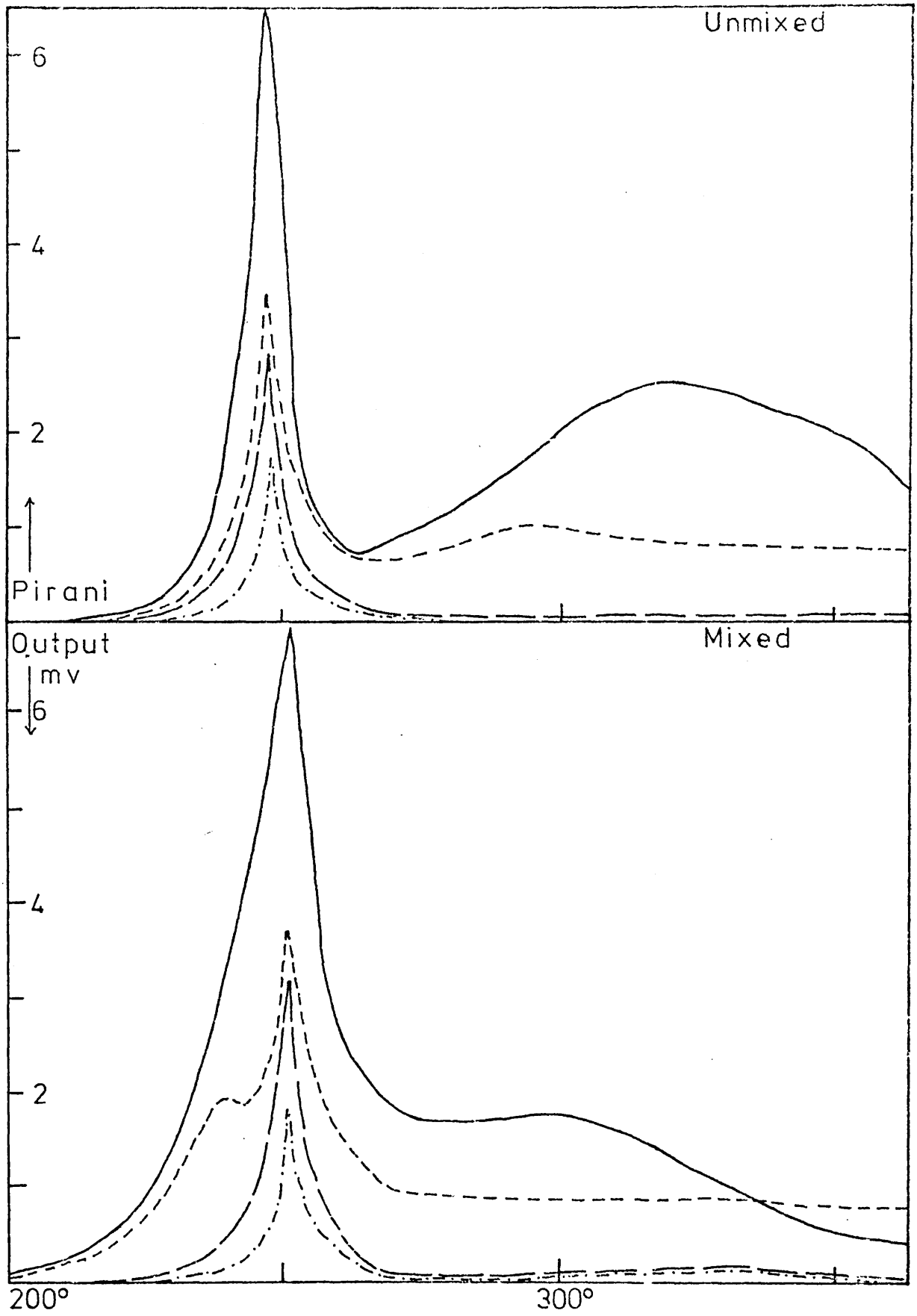


Figure (10.4). TVA traces for equal weights of AgAc and PMMA FR1 degraded simultaneously as (a) unmixed (b) mixed samples.
Powder samples, heating rate 5°C/min.

is considerably reduced in size at higher temperatures. The production of volatile material from AgAc is virtually unaffected, as may be seen from the behaviour of the -100° and -196°C traces. There is also evidence for production of a small amount of material non-condensable at -100° and -196°C later in the degradation.

The effect, on the degradation behaviour of the mixed system, of varying the ratio of the two components is shown in fig ure (10.5) for a 5:1 by weight ratio of PMMA : AgAc, and in figure (10.6) for a 10:1 by weight ratio. In both cases, the volatilization pattern of the mixed system indicates that the depolymerization of PMMA is being accelerated considerably and that the evolution of monomer is occurring rapidly at temperatures between 200° and 250°C. It was observed that similar results were obtained if the mixed system was degraded in the form of AgAc powder, dispersed in a film of PMMA cast from benzene solution.

Isothermal degradation at 240°C of unmixed and mixed samples gave TVA traces which are reproduced in figure (10.7). The trace for the unmixed system shows one complex peak which results from the production of some MMA monomer overlapping with the volatilization from AgAc. The trace for the mixed system exhibits a large volatilization peak which is caused mainly by the increased MMA monomer production, as can be seen by the limiting rate behaviour of the -75°C trace.

The outstanding feature of all these TVA traces is the vastly increased rate of production of MMA monomer early in the degradation from PMMA degraded in the presence of AgAc.

Volatiles Analysis.

Analysis of the volatile degradation products by infra-red spectroscopy showed that acetic acid, MMA and carbon dioxide were the principal products, with a trace of ketene. Also quantitative

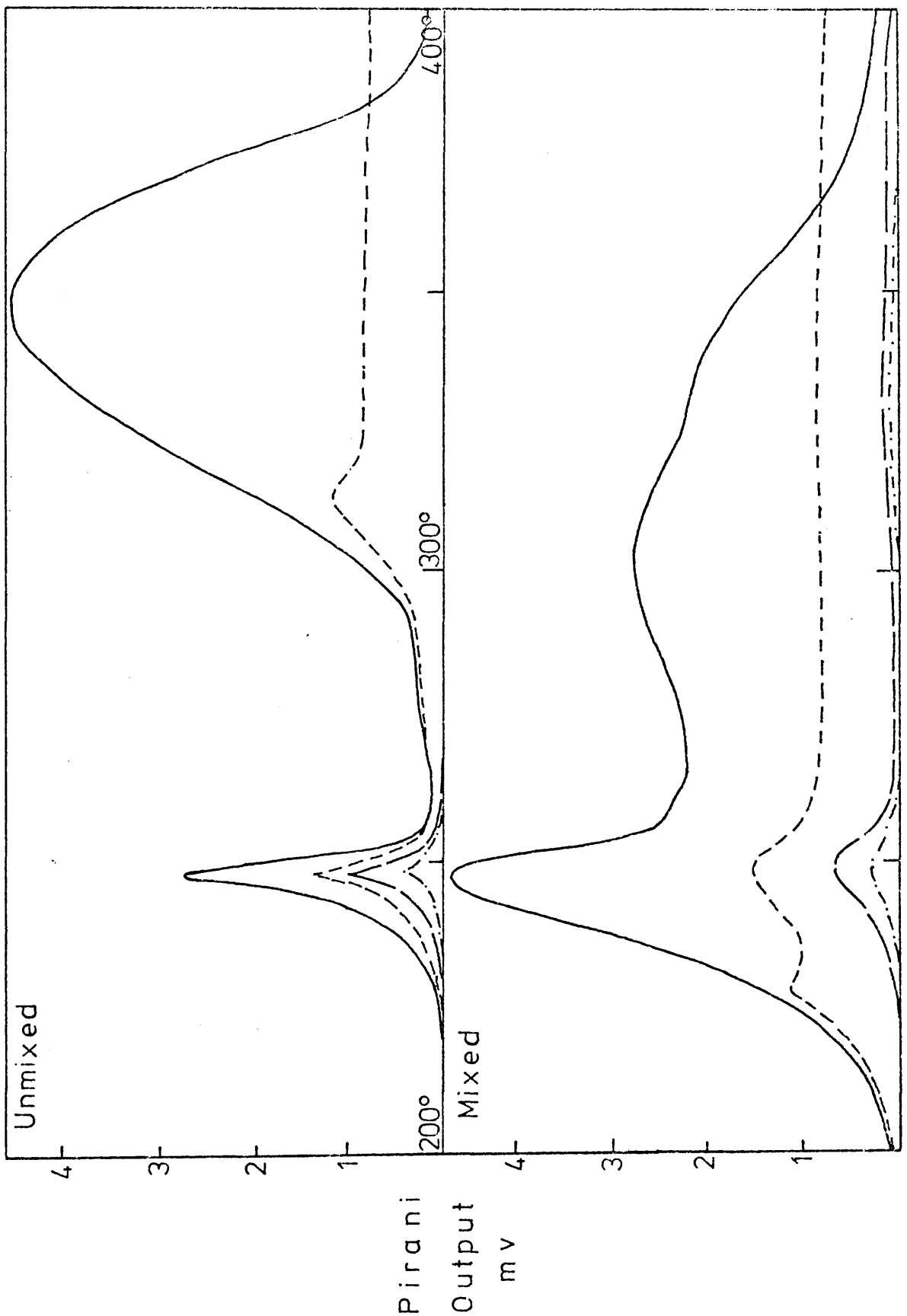


Figure (10.5). TVA traces for simultaneous degradation of AgAc and PMMA FR1 as (a) unmixed, (b) mixed powder samples. (1:5 by weight ratios of AgAc : PMMA). Heating rate 5°C/min.

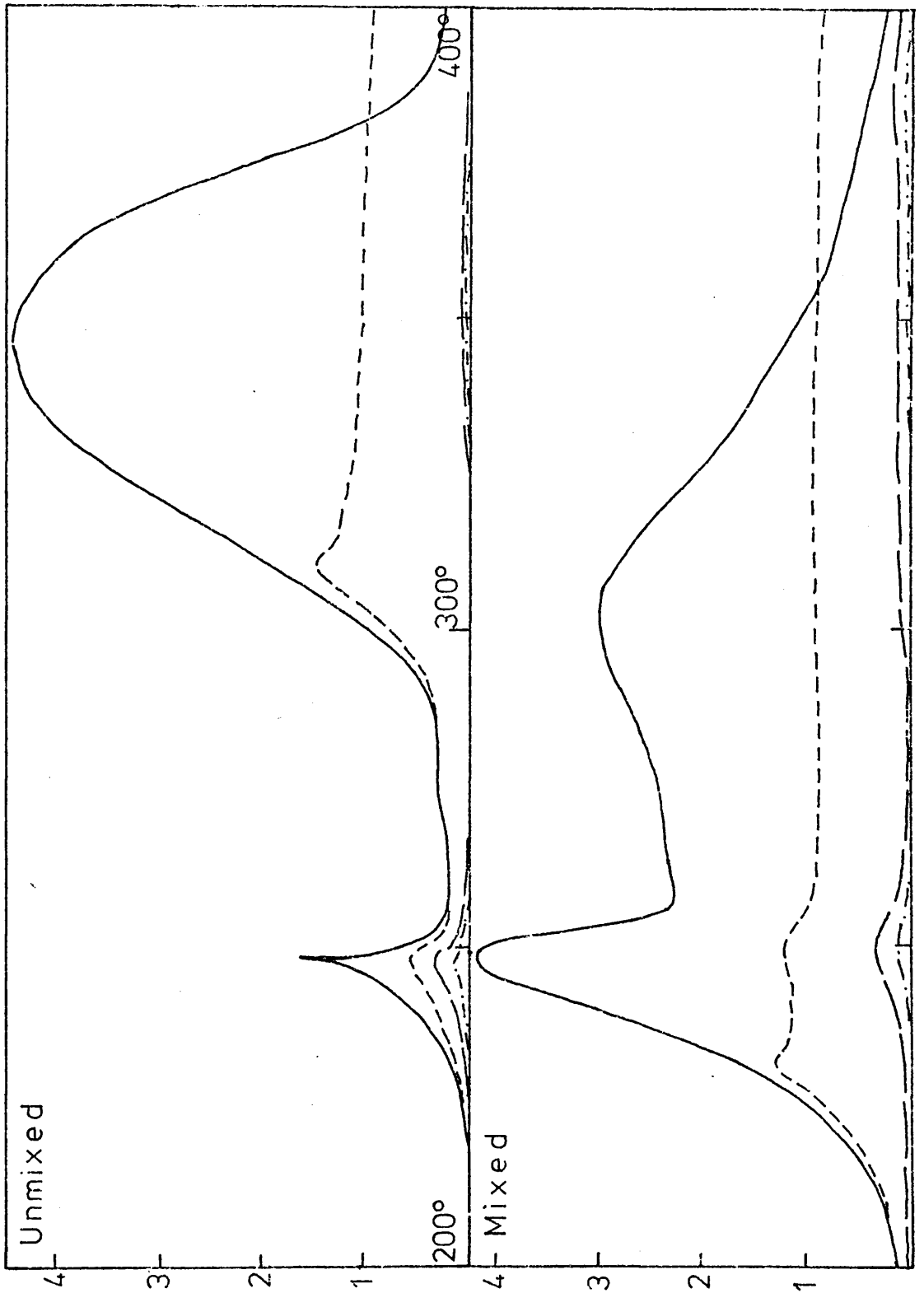


Figure (10.5). TVA traces for simultaneous degradation of AgAc and PMMA FR1 as (a) unmixed, (b) mixed powder samples (1:10 by weight ratios of AgAc : PMMA). Heating rate 5°C/min.

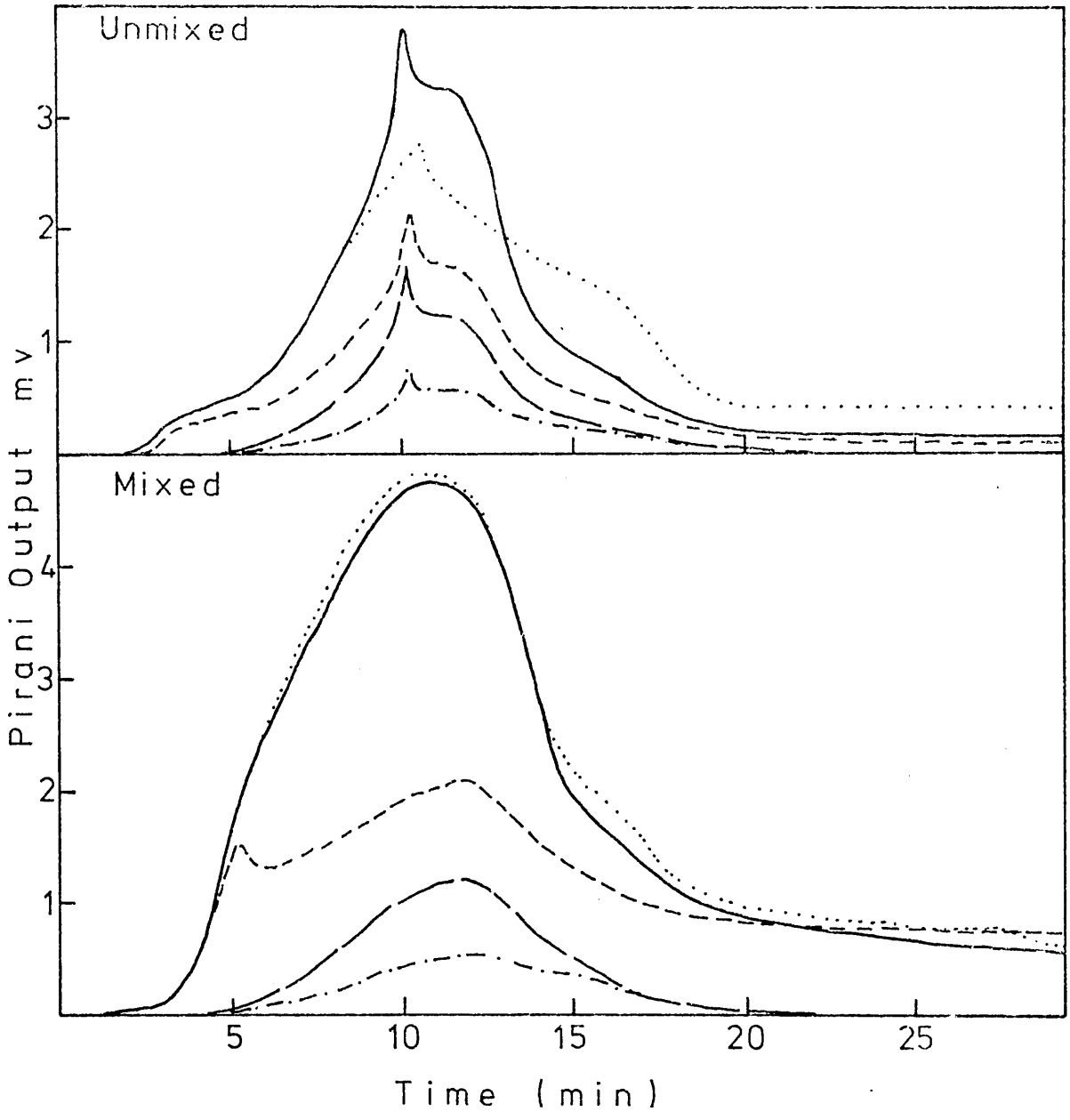


Figure (10.7). Isothermal TVA traces (240°C) for simultaneous degradation of equal amounts of AgAc and PMMA FR1, as (a) unmixed, (b) mixed, powder samples.

estimation of acetic acid by titration with standard alkali revealed that the amount of acid produced in the unmixed and mixed systems was identical.

Quantitative analysis of the rate of production of products from degradation at 207°C of the unmixed and mixed systems was carried out by GLC using the Perkin Elmer F11 Gas Chromatograph. Equal weights of PMMA and AgAc (100 mg of each substance) were degraded simultaneously as unmixed and mixed powder samples, the products collected, weighed and analysed as described previously, using n-propanol as internal standard and a column containing 13½% MEA and 6½% Di-2-Ethyl Hexyl Sebacate on Chromosorb at 75°C. It was found that for degradation at this temperature only acetic acid and MMA monomer were produced in quantities which could be estimated in more than trace amounts.

In figure (10.8) the total weight loss (as a percentage of the total original weight of sample) from the unmixed and mixed systems is plotted against time, and it can be seen that the rate of weight loss from the mixed system is considerably greater than that from the unmixed system. In figure (10.9) the rate of weight loss of MMA monomer (as a percentage of the original weight of PMMA) is shown for the mixed and unmixed systems, and it can be seen that the rate of production of MMA from the mixed system is considerably greater than that from the unmixed system, thus confirming the TVA evidence. The rate of production of acetic acid from the mixed system is only very slightly greater than that from the unmixed system, as may be seen in figure (10.10), although this may not be of much significance.

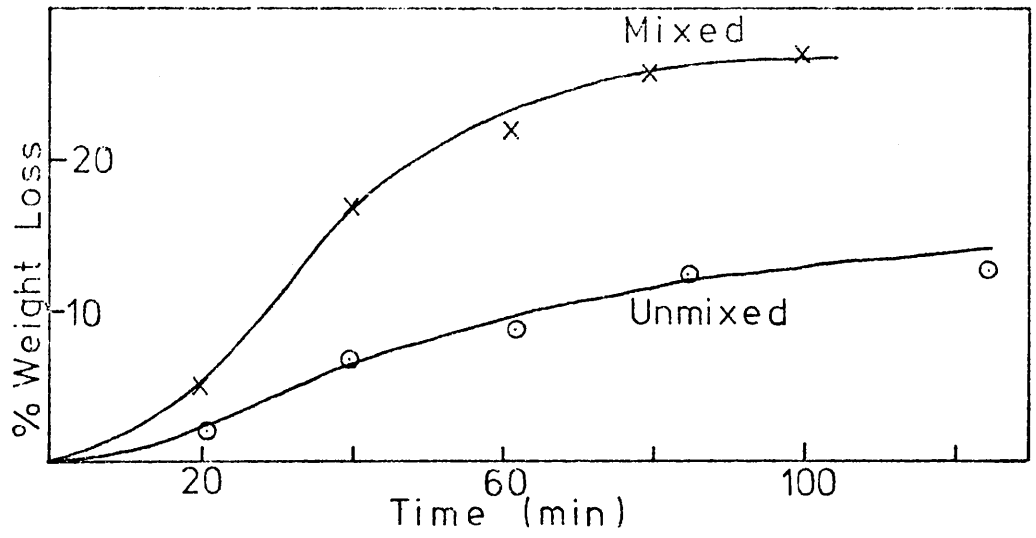


Figure (10.8). Weight loss (GLC) from simultaneous degradation at 207°C of equal amounts of AgAc and PMMA FR1 as (a) unmixed (b) mixed samples.

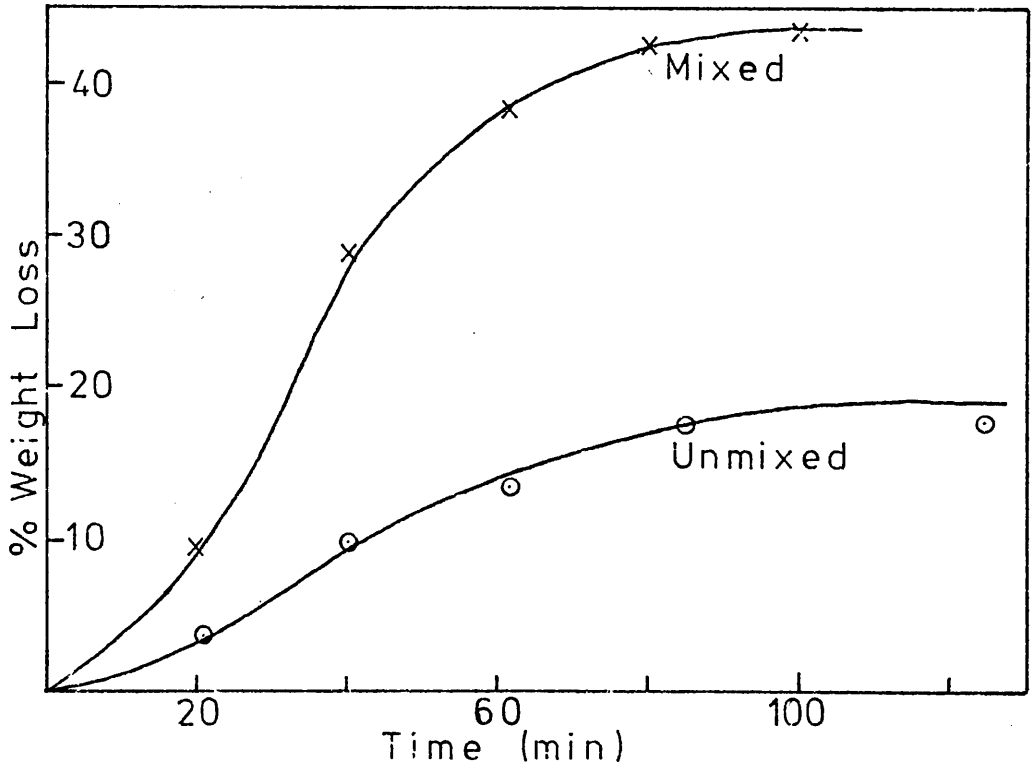


Figure (10.9). Production of MMA (as % weight loss of PMMA) from simultaneous degradation at 207°C of equal amounts of AgAc and PMMA FR1 as (a) ummixed, (b) mixed samples.
Estimations by GLC.

RESIDUE ANALYSIS.

A 50 mg sample of PMMA was degraded at 5°C/min to 270°C, cooled and extracted with benzene. A film was cast on a sodium chloride disc and an infra-red spectrum obtained which was identical to the original sample. The TVA trace of the extracted material is shown in figure (10.11) and it is very similar to that for the original sample.

A 50 mg sample of PMMA was degraded under similar conditions as a mixed powder system with an equal weight of AgAc, and, after cooling, the polymer was extracted with benzene, filtered and an infra-red spectrum and TVA trace obtained as before. The infra-red spectrum was again identical to that for the original PMMA sample, but the TVA trace, shown in figure (10.11), is different to that for the PMMA sample degraded alone. It can be seen that the amount of material extracted from the mixed system is smaller than from the unmixed system, but this is expected from previous observations that the weight loss of PMMA from the mixed system is much greater than from the unmixed. However, the overall shape of the two traces is also completely different, and even from the small amount of polymer obtained from the mixed system, the proportion of MMA evolved below 300°C (due to chain end initiated depolymerization) is greater for the sample extracted from the mixture.

EFFECT OF UV IRRADIATION ON PMMA-AgAc BLENDS.

Because of the remarkable acceleration of PMMA breakdown during degradation with AgAc, the effect of UV irradiation on mixtures of PMMA and AgAc was investigated. A 50 mg film of PMMA in silica tubes was subjected to six hours irradiation (2537 Å) at 20°C, under vacuum. The polymer was extracted with benzene and examined by infra-red spectroscopy and TVA. From analysis by infra-red the sample was shown to give a spectrum identical to that for the original sample.

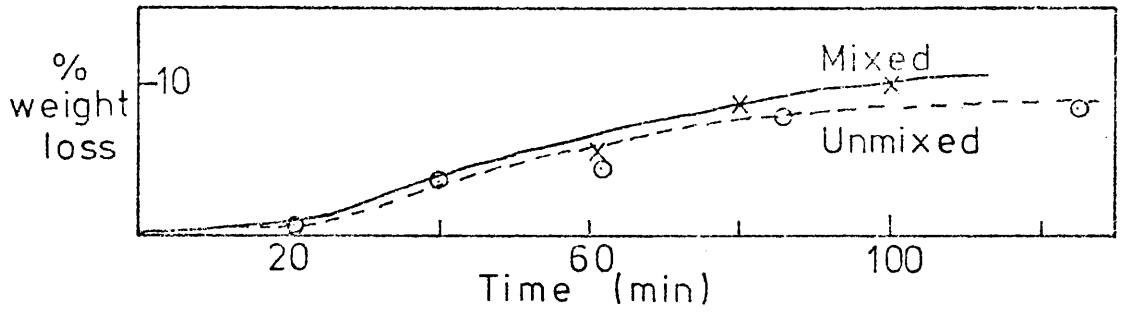


Figure (10.10). Production of acetic acid (as % weight loss of AgAc) from simultaneous degradation at 207°C of equal weights of AgAc and PMMA FR1 as, (a) unmixed, (b) mixed samples. Estimations by GLC.

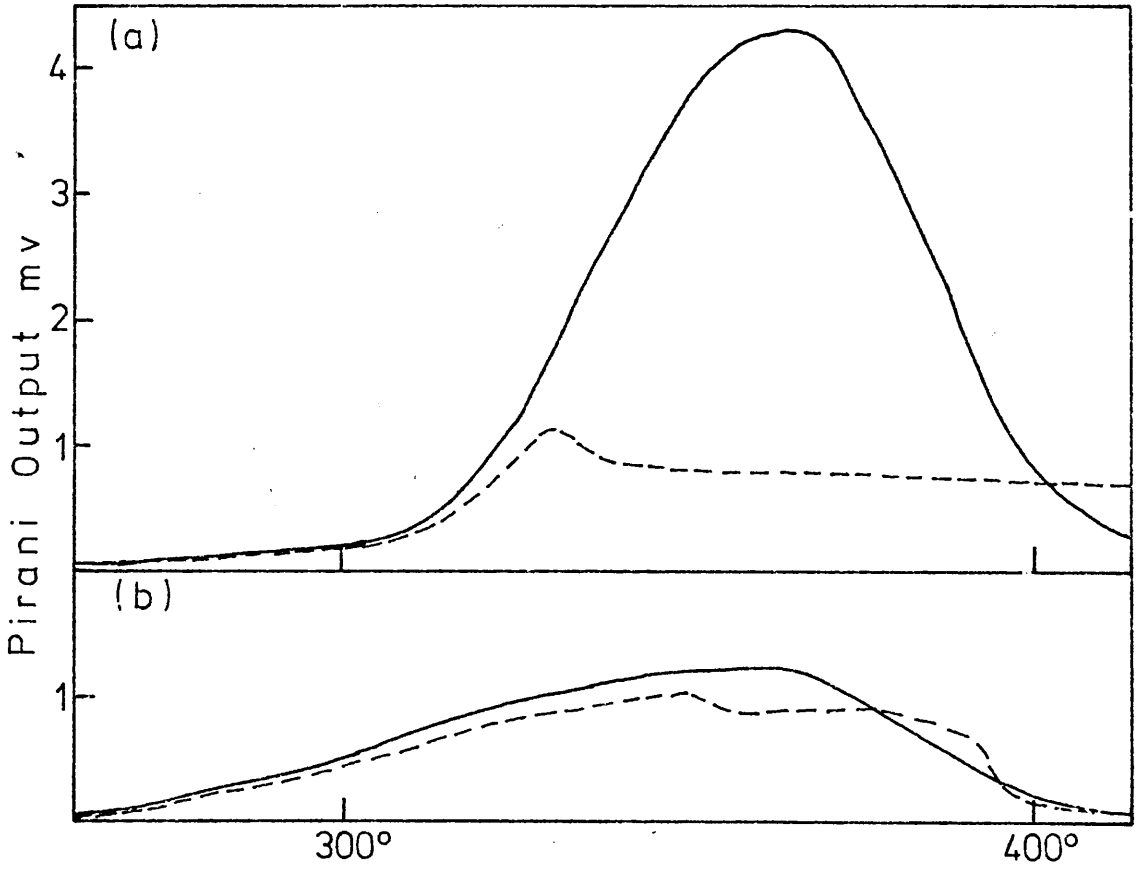


Figure (10.11). TVA traces of PMMA FR1 samples extracted from partial degradation to 270°C (at 5°C/min) of (a) PMMA alone, (b) PMMA with an equivalent amount of AgAc.

The TVA trace, reproduced in figure (10.12), shows a small peak for chain end initiated depolymerization compared to an extremely small shoulder for the original sample. This is to be expected since photodegradation of PMMA results in chain scission (88) causing an increase in the concentration of unsaturated double bonds. This decrease in stability of PMMA on UV irradiation has been demonstrated previously (32).

A 50 mg film of PMMA with an equal weight of AgAc dispersed within it, was subjected to similar photodegradation. The residue which was brown in colour, was extracted as before and examined by infra-red spectroscopy and TVA. The infra-red spectrum was identical to that for the original sample. The TVA trace for this sample, shown in figure (10.12), also exhibits a decrease in stability, but the overall amount of material is also less than from the sample which had been photodegraded alone. This latter effect may result from incomplete extraction or from an increased amount of monomer produced during photodegradation of the unmixed sample. However the effect of UV irradiation on the mixtures under these conditions is insignificant compared to the effect of thermal degradation.

DISCUSSION.

The marked acceleration of depolymerization of PMMA when it is degraded as a mixture with AgAc results in the production of high yields of monomer at low temperatures. This indicates a very significant interaction between AgAc and PMMA during degradation and would seem to indicate that AgAc, on decomposition, must be producing a species capable of inducing radical depolymerization within PMMA. It is likely that PMMA is subjected to a radical attack, leading to subsequent chain scission and depropagation, via a hydrogen abstraction process similar to that described in chapter one for the interaction of a

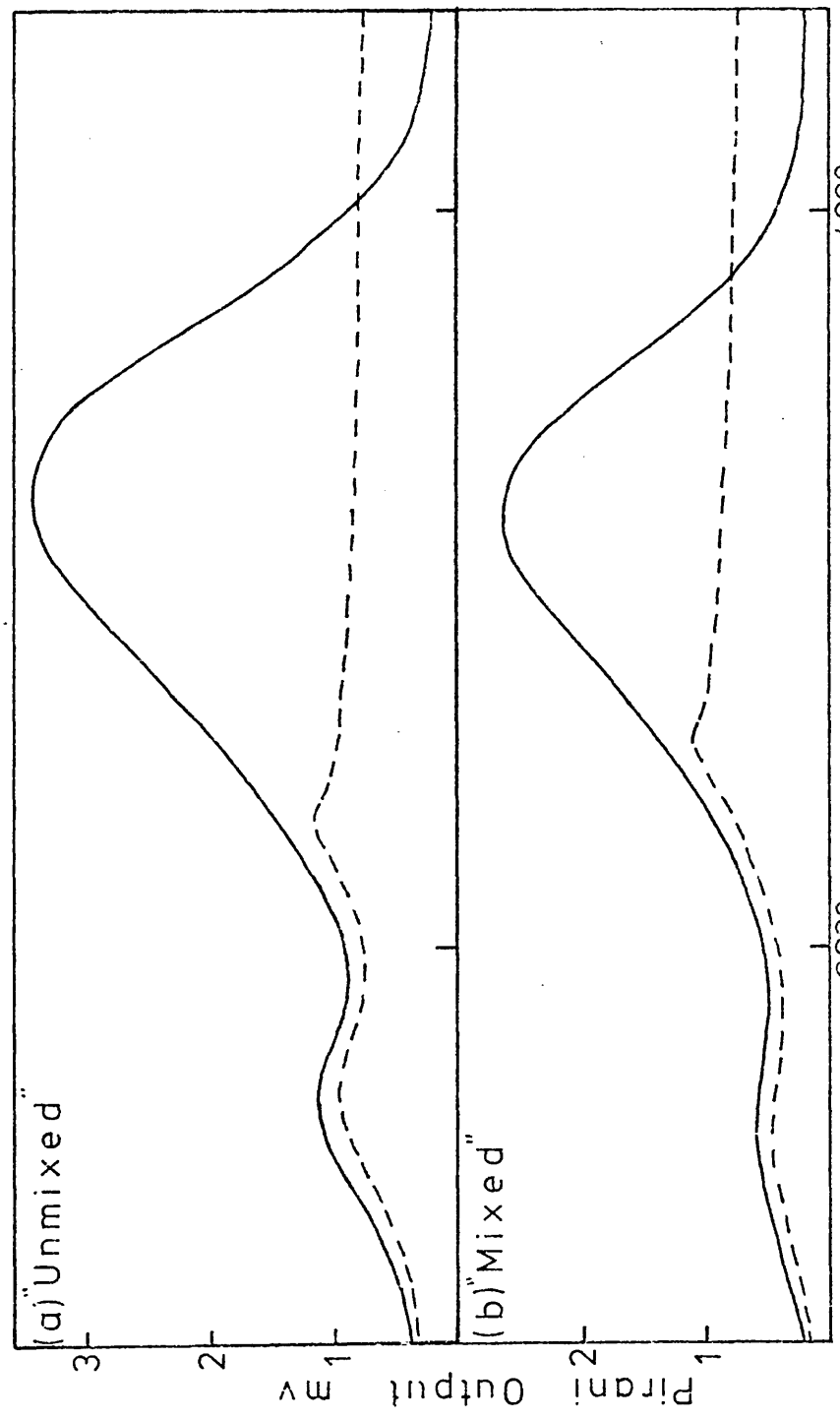


Figure (10.12). TVA traces of PMMA FR1 (50 mg film) photodegraded under vacuum at 20°C (a) alone, (b) with an equal amount of AgAc. Heating rate 5°C/min.

of a chlorine radical with PMMA. To determine the nature of the interacting radical, it is necessary to consider possible reaction pathways for the decomposition of AgAc, and these must take into account the various species which result from the degradation; viz, acetic acid, carbon dioxide, ketene, carbon monoxide and metallic silver.

The maximum "theoretical" yield of acetic acid from AgAc is 75% and it is unlikely at these temperatures of degradation, that the discrepancy between the observed (61%) and "theoretical" acetic acid yields, is due to decomposition of acetic acid. The "theoretical" yield of acetic acid can be calculated using the following reaction sequence :-

$$4\ (C_2H_3O_2Ag) \longrightarrow 3\ CH_3COOH + 4Ag + C_2H_2O_2$$

This reaction sequence can yield other identified reaction products from different formulations of the $C_2H_2O_2$ group :-

$$C_2H_2O_2 \longrightarrow CO_2 + CH_2^{\cdot\cdot}$$

$$\xrightarrow[+2Ag]{or} CH_2^{\cdot\cdot}{=}C{=}O + Ag_2O$$

$$\xrightarrow{or} 2CO + H_2$$

There are, however, several possible mechanisms for the formation of acetic acid and the other minor products, two of the more likely of which are outlined below :-

A.
$$CH_3COOAg \longrightarrow CH_3COO\cdot + Ag\cdot$$
$$CH_3COO\cdot + CH_3COOAg \longrightarrow CH_3COOH + \cdot CH_2COOAg$$
$$\cdot CH_2COOAg \longrightarrow CH_2^{\cdot\cdot}{=}C{=}O + AgO\cdot$$
$$\xrightarrow{or} CH_2^{\cdot\cdot} + CO_2 + Ag$$
$$\xrightarrow{or} CH_2^{\cdot\cdot} + CO + AgO$$
$$\xrightarrow{or} H_2 + 2CO + AgO$$
$$AgO\cdot + Ag\cdot \longrightarrow Ag_2O$$

B.

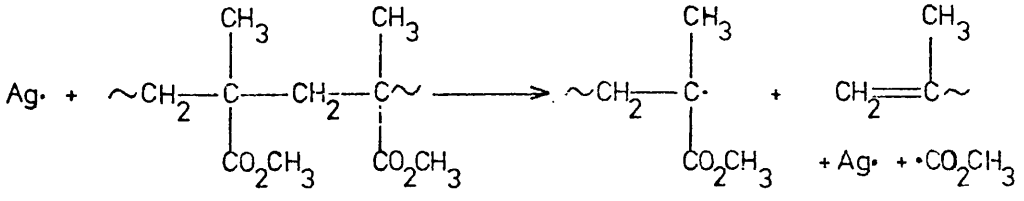
$$CH_3COOAg \longrightarrow CH_3^{\bullet} + {}^{\bullet}CO_2Ag$$

$$CH_3^{\bullet} + CH_3COOAg \longrightarrow CH_2^{\bullet} + CH_3COOH + Ag^{\bullet}$$

$${}^{\bullet}CO_2Ag \longrightarrow CO_2 + Ag^{\bullet}$$

$$\xrightarrow{\text{or}} CO + AgO^{\bullet}$$

To identify the radical or radicals responsible for the interaction from the above complex reaction sequences is difficult, but because of the heterogeneous nature of the AgAc - PMMA mixture, it seems unlikely that the organic radicals discussed above would be sufficiently long-lived to be capable of traversing phase boundaries in the extremely heterogeneous mixed powder system. However, since at the end of degradation it was observed that a film of metallic silver completely covered the base and also much of the walls of the degradation tube, it is possible that migrating silver radicals are responsible for the interaction leading to accelerated breakdown of PMMA :-



The mechanism of this reaction may involve attack of the silver radical at the carbonyl group of the methacrylate ester.

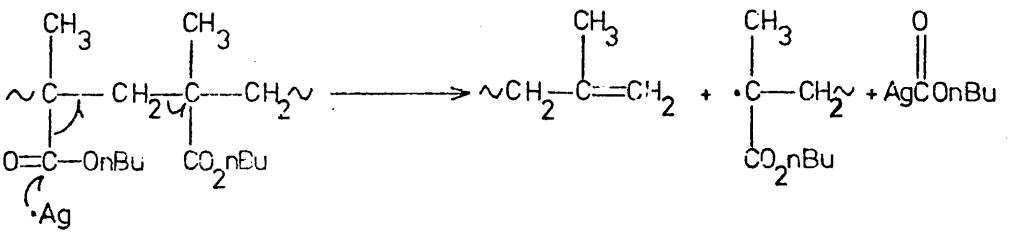
THE DEGRADATION OF SOME OTHER POLYMERS IN THE PRESENCE OF SILVER ACETATE.

POLY (n - BUTYL METHACRYLATE).

The pronounced increase in monomer production early in the degradation process, which occurs when PMMA is degraded with AgAc, might also be expected with PBMA which depolymerises to monomer as the major degradation reaction (5).

The TVA trace for simultaneous degradation of equal weights of AgAc and PBMA in an unmixed condition is shown in figure (10.13). The sharp peak for AgAc can be identified, but that there is also some monomer production from PBMA occurring at this stage can be seen from the substantial amount of material condensable at -75°C, but non-condensable at 0°C. The second peak results from the principal region of monomer production from PBMA, as may be observed from the limiting rate behaviour of the -45°C trace, and there is also some evolution of butene (non-condensable at -75° and -100°C) from decomposition of the PBMA ester group.

In the trace for the mixed system, shown in figure (10.14), there is evidence for increased volatiles production at low temperatures. The pattern of the traces for the different cold traps and the behaviour of the -45°C trace which exhibits a limiting rate effect, suggests that this increased volatilization is due to BMA monomer. Also the peak above 300°C, which corresponds to the principal region of monomer production is reduced in size in the mixed trace compared to the unmixed trace. Thus it appears that there is an acceleration of monomer production from PBMA and it is reasonable to suggest that the mechanism of interaction is similar to that proposed for the PMMA system.



There is also an extra peak in the mixed trace just below 400°C, due to the production of substantial amounts of material, some of which is non-condensable at -75°C, some at -100°C and some at -196°C. The material non-condensable at -196°C, which is also produced in small quantities from the unmixed system, probably results from

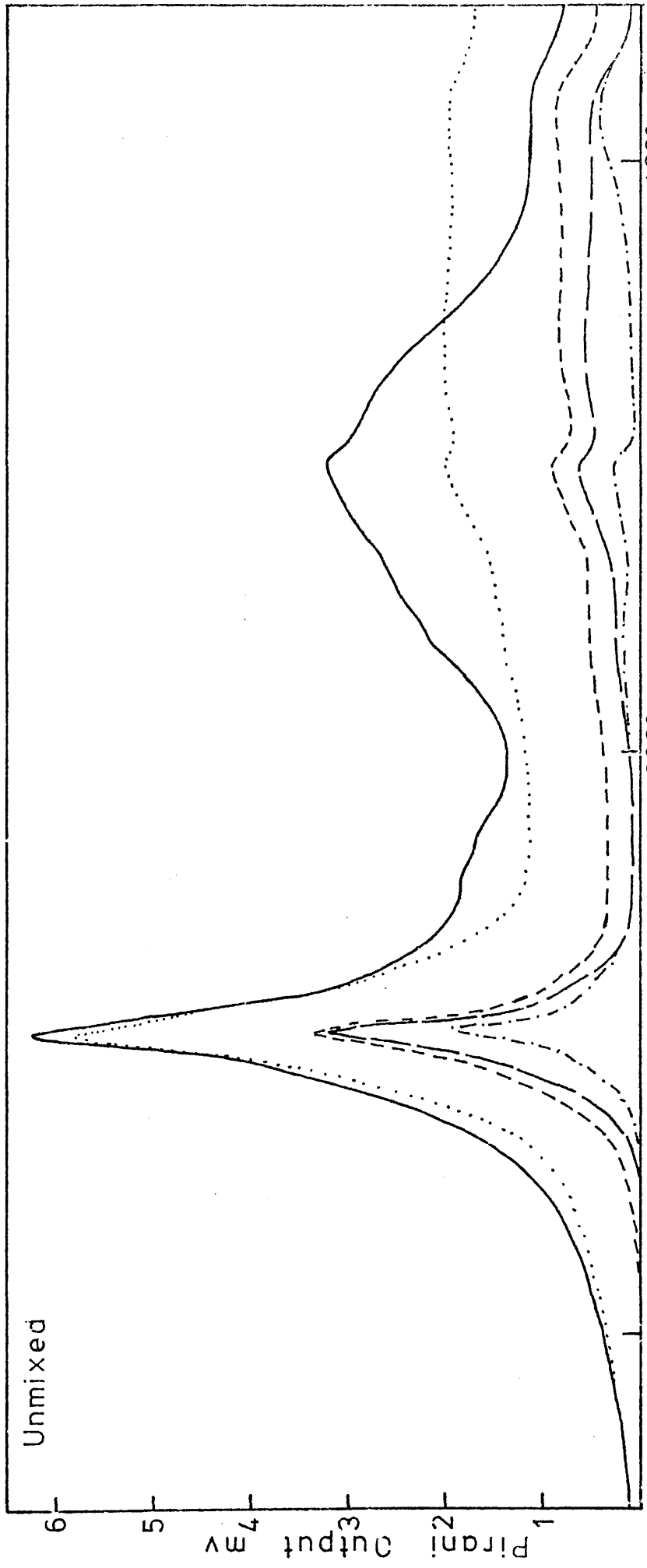


Figure (10.13). TVA trace for simultaneous degradation of equal amounts of AgAc and PBMA (50 mg of each) in an unmixed condition. Heating rate 5°C/min.

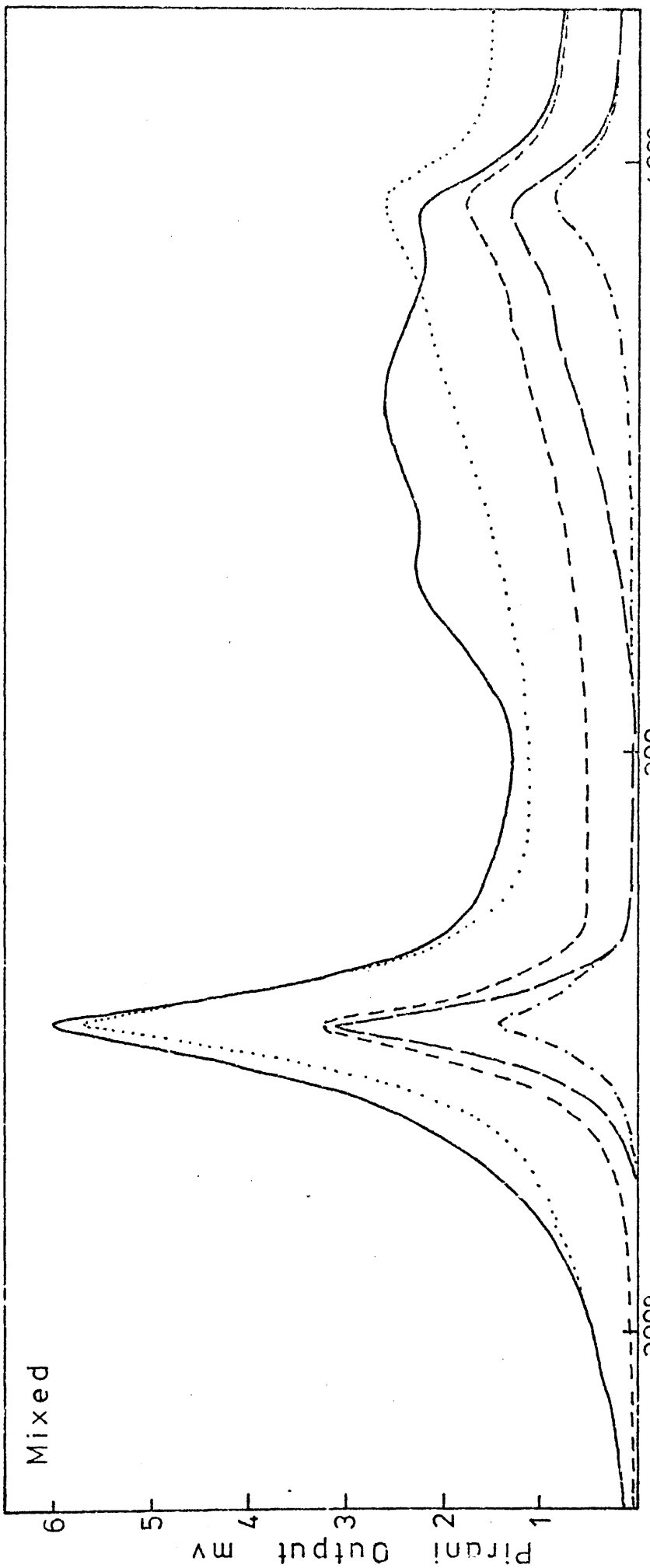


Figure (10.14). TVA trace for simultaneous degradation of equal amounts of AgAc and PBMA (50 mg each) in a mixed condition. Heating rate 5°C/min.

decomposition of polymethacrylic acid type structures (77). It is interesting to note that this increase in production of highly volatile material at higher temperaturesdoes not occur in the AgAc - PMMA system, and hence it is unlikely that it is caused by an increase in polymethacrylic acid (and subsequently anhydride) units arising from interaction of the acetic acid with the methacrylate ester groups. An increase in these acid units could result from increased butene production from PBMA by interaction of a radical species with one of the hydrogen atoms of the n - butyl group. One other explanation is that the volatile products arise from decomposition of the silver compound, Ag CO_2 n Bu, which might result from interaction of silver radicals with the PBMA.

POLYACRYLONITRILE

The TVA curves for simultaneous degradation of equal weights of AgAc and PAN in an unmixed and mixed condition are shown in figure (10.15). The unmixed trace shows the two typically distinct sharp peaks for AgAc decomposition and evolution of volatiles during cyclisation of PAN. The trace for the mixed system also has two corresponding peaks, but the one at lower temperatures associated with AgAc decomposition is broader and appears to have a larger amount of material non-condensable at 0° and $-45^{\circ}C$ but condensable at $-75^{\circ}C$, than the peak for AgAc in the unmixed system.

The nature of the interaction in this system is difficult to elucidate, but it may be that acrylonitrile monomer from a limited amount of chain scission and depolymerization is responsible for the increased volatilization behaviour at lower temperatures. Chain scission of PAN could occur by a mechanism similar to that for chain scission in the methacrylate esters of PMMA and PBMA, viz. attack on the - C≡N group of PAN by silver radicals. The extent

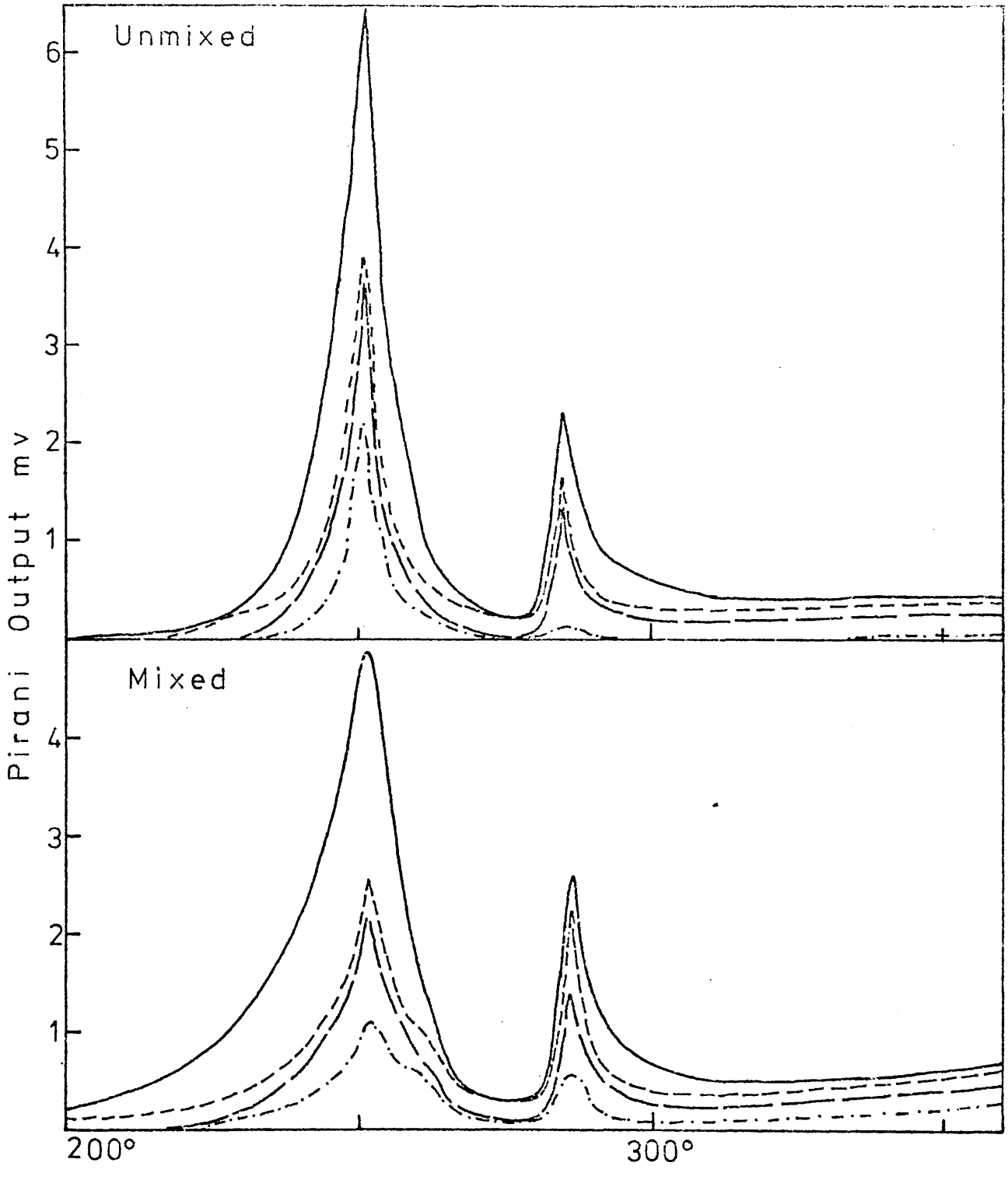


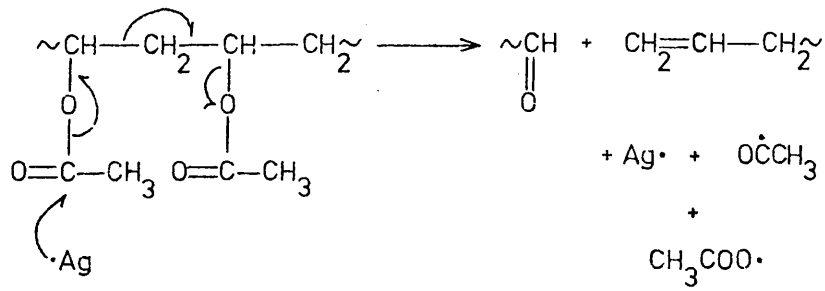
Figure (10.15) TVA traces for equal amounts of AgAc and PAN (50 mg each) degraded simultaneously in (a) an unmixed (b) a mixed condition as powders. Heating rate 5°C/min.

of this interaction appears to be limited since volatilization behaviour of the PAN during cyclisation is similar in the mixed and unmixed systems.

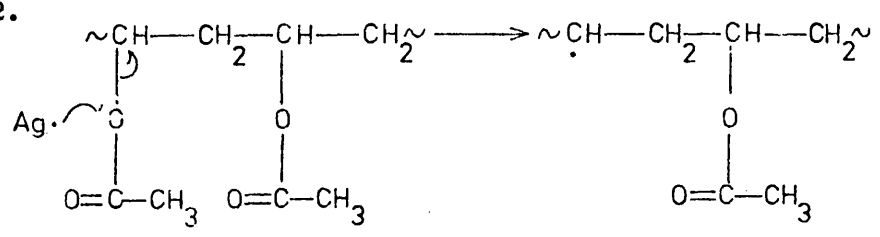
POLY (VINYL ACETATE)

TVA traces for simultaneous degradation of equal amounts of AgAc and PVA in an unmixed and mixed condition are shown in figures (10.16) and (10.17) respectively. The "unmixed" trace exhibits two peaks, for AgAc decomposition, and deacetylation of PVA, the latter occurring at higher temperatures. In the "mixed" trace, the AgAc peak is reduced in height, but is broadened considerably and has a lower initiation temperature. Also, there is evidence of increased production of material volatile at 0^{o} and $-45^{o}C$, but condensable at $-75^{o}C$, as well as a decrease in the amount of material evolved at the region of PVA deacetylation, which appears to indicate that the deacetylation of PVA is being accelerated in the presence of AgAc. Two possible routes are suggested for the interaction of silver radicals with PVA :-

1.



2.



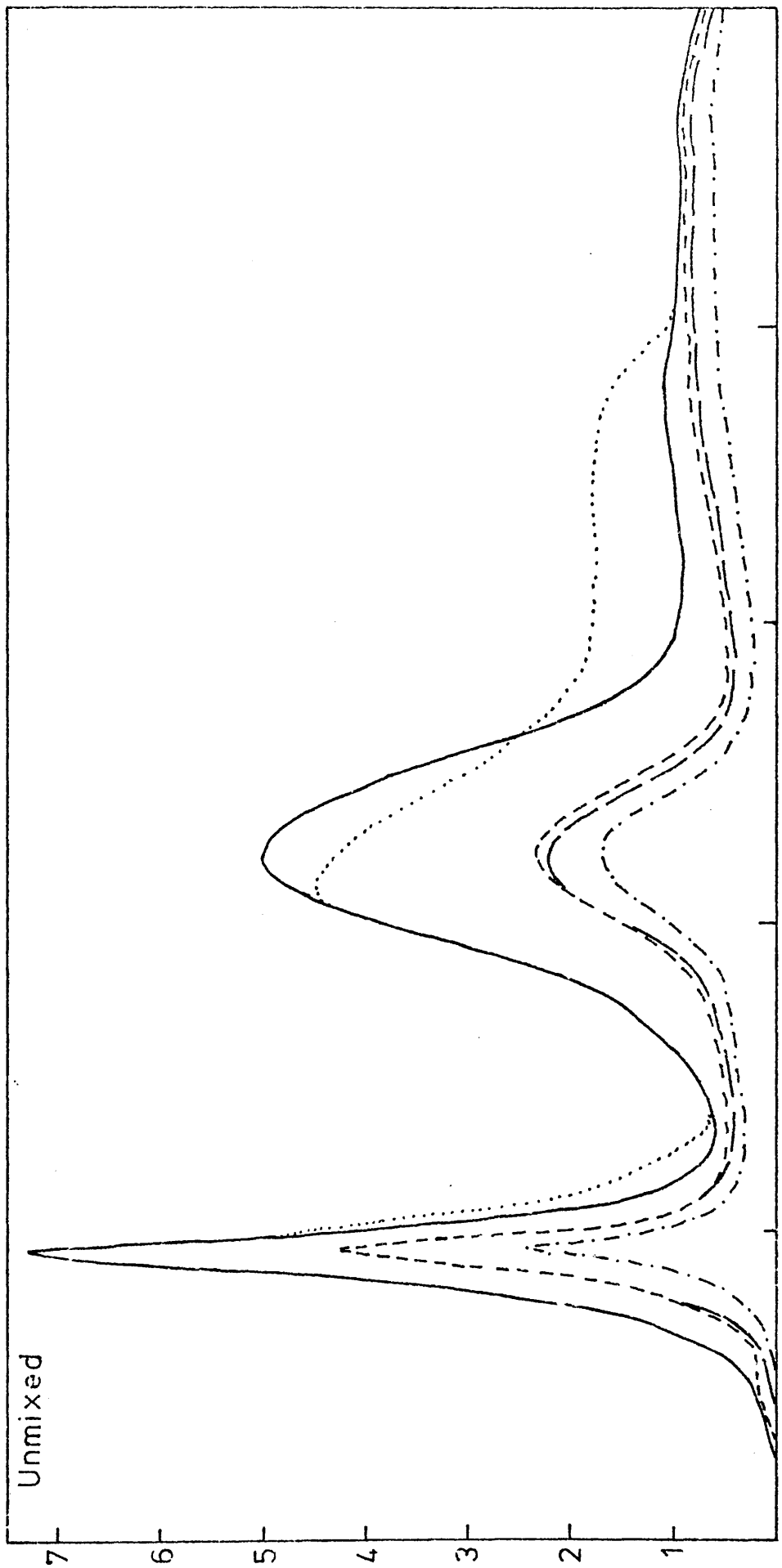


Figure (10.16). TVA trace for simultaneous degradation of equal amounts of AgAc and PVA (BDH) (50 mg of each), in an unmixed condition. Heating rate 5°C/min.

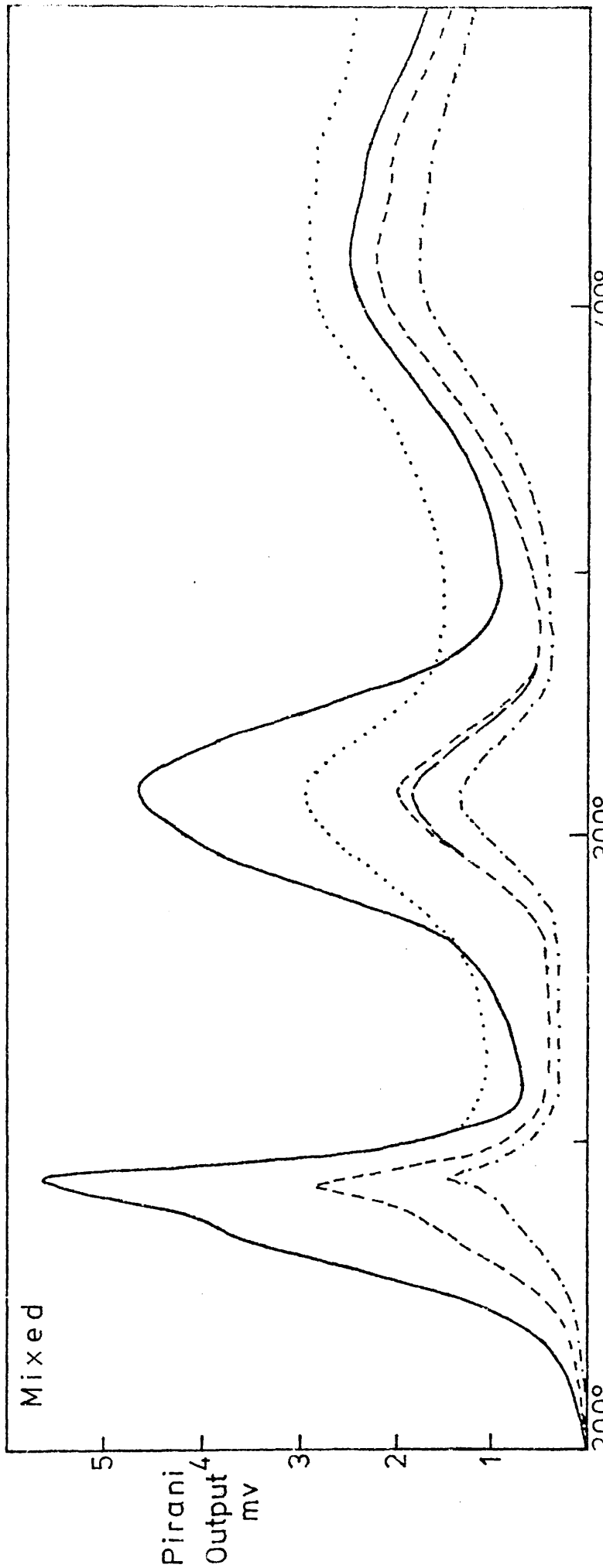


Figure (10.17). TVA trace for simultaneous degradation of equal amounts of AgAc and PVA (BDH), (50 mg of each), in a mixed condition. Heating rate 5°C/min.

The first route causes chain scission and produces an acetate radical which can initiate deacetylation of PVA, while the second route produces AgAc and a PVA radical.

The other major difference between the mixed and unmixed traces is the appearance above 400°C in the mixed system of a large peak, which, for the most part, is due to products non-condensable at -196°C. This is the region of breakdown of the carbonaceous PVA residue and this effect may be caused by the decomposition of structures like the carbonyl group shown in the first reaction route above.

MISCELLANEOUS OTHER POLYMERS.

TVA traces for mixed and unmixed samples of AgAc with poly (alpha methyl styrene) were identical in all respects, thus indicating that AgAc had no effect on the decomposition of PAMS. This is surprising in view of the fact that PAMS, like PMMA, depolymerises almost totally to monomer on degradation. However, PAMS does not have a polar centre like the carbonyl of the methacrylate ester, where the silver radical can attack.

TVA investigations of the degradation of the AgAc - polystyrene system also revealed no interactions, as would be expected by comparison with the PAMS system.

Mixtures of AgAc with PVC and Alloprene revealed no interactions during degradation, neither the dehydrochlorination reaction nor the breakdown of the carbonaceous residue being affected. This is surprising, since it might be expected that the silver radicals would be effective in attacking C-Cl bonds, producing radical centres in the polymer chain.

SUMMARY.

Degradation of polymers in the presence of AgAc can result in various effects, of different extents, on the decomposition of the

polymer. The depolymerization of PMMA is considerably accelerated, that of PBMA less so, while the depolymerization of PS and PAMS is unaffected, by degradation in the presence of AgAc.

The effect of AgAc on the decomposition of PVA is reflected by an increased rate of deacetylation and an increased amount of highly volatile products from breakdown of the polyene residue. In contrast, the dehydrochlorination of PVC and alloprene is unaffected by degradation with AgAc while there is increased volatilization from the PAN system.

These phenomena are consistent with interaction of silver radicals with polar groups within the polymer chain, although the C-Cl bonds of PVC and alloprene are exceptions to this hypothesis.

CHAPTER ELEVEN

THE DEGRADATION OF METHYL METHACRYLATE - METHACRYLIC ACID COPOLYMERS

The production of anhydride structures in PMMA during degradation in the presence of PVC (21), PC (27) and PVA (chapter three) has been discussed, and several possible mechanistic routes suggested for the reaction. It was indicated (21) that further evidence for the mechanism of this reaction could be obtained from an investigation of the degradation of (methyl methacrylate) - (methacrylic acid) copolymers, and hence this work was undertaken.

INTRODUCTION.

The degradation of poly (methacrylic acid) (PMAA), which was discussed briefly in chapter one, was first carried out by Bresler, Koton and co-workers (89) who found that the cyclic structures produced when water is liberated from PMAA are very much more thermally stable than the parent substance.

Grant and Grassie (15) studied the thermal decomposition of PMAA in greater detail and found that two separate reactions occur. The minor one is depolymerization which results in small yields of monomer (0.2%), while the major one is anhydride formation by elimination of water between pairs of carboxylic acid groups. The residual product was shown to be predominantly linked, six-membered anhydride rings with occasional cross-links.

In an investigation of the degradation of poly (t - butyl methacrylate), Grant and Grassie (11) briefly examined a MMA - MAA copolymer and obtained a stable polymer after prolonged heating at 200°C. Infra-red scpectoscopy showed the acid to be completely

converted into anhydride, and an exchange reaction between acid and ester groups was proposed to explain the reaction of isolated acid groups. Anhydride formation was also found in the thermal degradation of poly (n - butyl methacrylate) by ester decomposition of the n - butyl methacrylate group, yielding but - 1 - ene, and residual methacrylic acid groups in the polymer chain (77, 84).

EXPERIMENTAL

Brief details of the preparation and history of the homopolymers and copolymers used in this work are shown in Tables (10.1) and (10.2) respectively.

Preparation of the MMA - MAA Copolymers.

(a) Monomers:- Methacrylic acid (Koch Light) was distilled under vacuum in the presence of inhibitor (to prevent polymerization). Methyl methacrylate (I.C.I. Ltd) was shaken with dilute NaOH to remove inhibitor, washed several times with distilled water and dried over $CaCl_2$.

(b) Filling of dilatometers:- Methacrylic acid was placed directly into the dilatometers containing the initiator, since it was found to polymerize in the vacuum line during distillation from the reservoir to the dilatometer. It was degassed in the presence of a small amount (less than 1 mg.) of inhibitor (diphenyl picryl hydrazyl). Methyl methacrylate was degassed, distilled into a reservoir, and then into the dilatometer containing the degassed methacrylic acid.

(c) Polymerizations :- These were carried out at 50°C to less than 5% conversion, by which extent, the polymer had precipitated from the mixture of monomers and certain precautions had to be taken against the possibility of explosion.

TABLE (11.1)

HOMOPOLYMER SAMPLES

Sample	History	$\bar{M}n$
PMAA (1)	Bulk polymerization in air at 20°C	-
PMMA (FR2)(2)	Bulk polymerization at 80°C using 4% AIBN	28,000
PMMA (FR3)(1)	Bulk polymerization at 60°C using 0.1% AIBN	595,000

(1) Prepared by Dr. I.C. McNeill.

(2) Prepared by Dr. M.A.J. Mohammed.

TABLE (11.2)

COPOLYMER SAMPLES

Sample	History	Mole % MAA
MMA - MAA 1	Bulk polymerizations at 50°C using 0.1% AIBN	10%
MMA - MAA 2		19%
MMA - MAA 3		33%
MMA - MAA 4		75%

(d) Isolation and purification of copolymers:- The copolymers were precipitated in petroleum ether, from chloroform solution for those of lowest methacrylic acid content, and from absolute alcohol solution for the 75% copolymer.

(e) Copolymer composition:- Reactivity ratios calculated by Smets and Van Gorp (90) were used ($r_{MMA} = 0.345$, $r_{MAA} = 0.956$) and the acid content of the copolymer determined by titration with standard NaOH, using phenolphthalein as indicator.

RESULTS AND DISCUSSION.

THERMAL VOLATILIZATION ANALYSIS.

The TVA trace for PMAA is reproduced in figure (11.1), and is identical to that obtained by McNeill (34), who interpreted it in the following way. The slow release of volatile material, which commences as soon as the temperature begins to rise, is due to the release of water absorbed by the polymer (the low plateau of the -75°C trace is characteristic of water (32)). At 200°C more extensive volatilization occurs, indicating that greater amounts of water are being produced. The almost concurrent evolution of a material volatile at -100°C (with consequent displacement of the -75°C trace until this volatilization is complete), is due to the precipitant ether. Water evolution has ceased at a temperature just above 300°C since the 0° and -45°C traces both return to the baseline. At this temperature, further volatilization occurs yielding carbon dioxide, carbon monoxide and methane (both the latter are volatile at -196°C). Figure (11.2) illustrates the early region of degradation, up to 275°C, showing more clearly some of the points mentioned above.

TVA traces for the four MMA - MAA copolymers are shown in

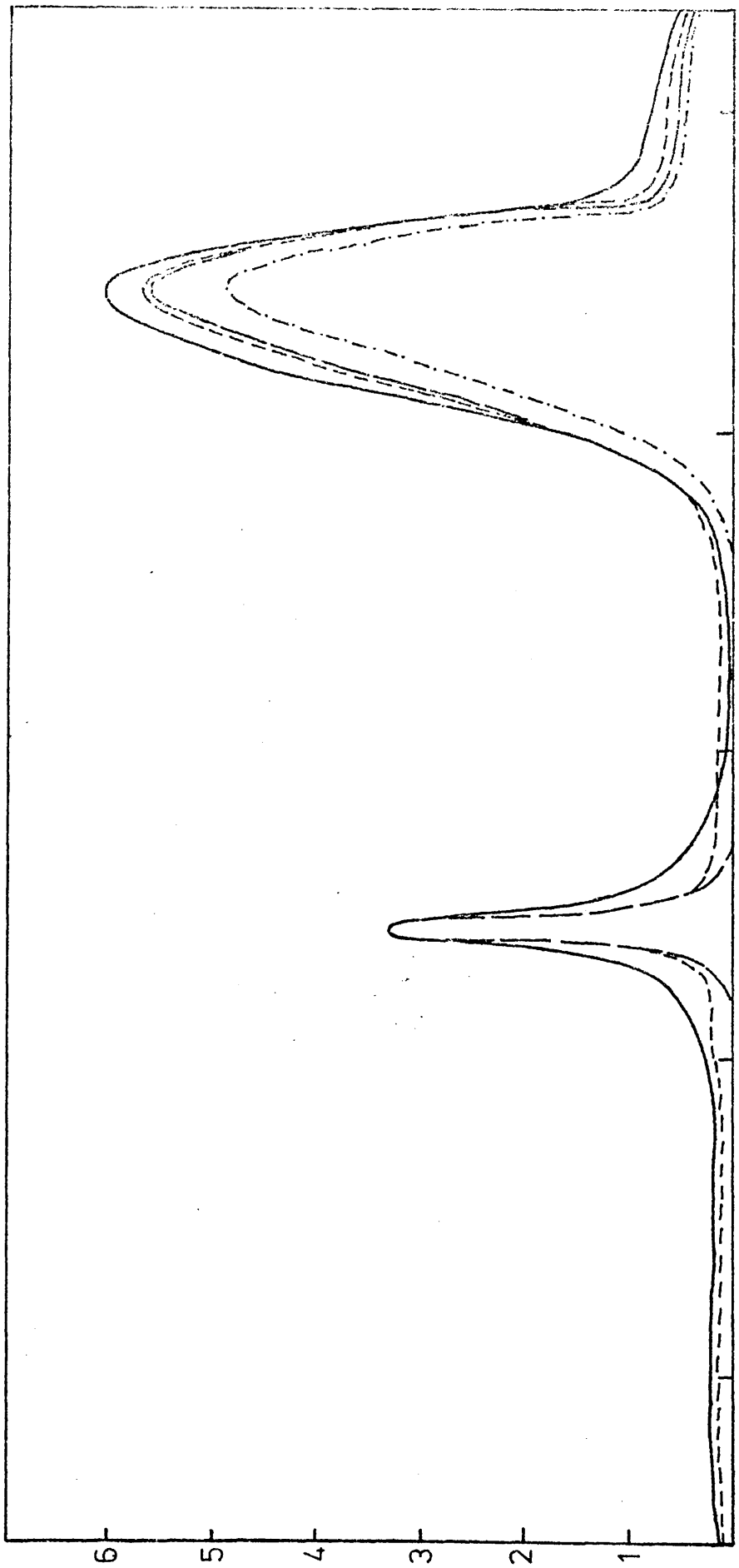


Figure (11.1). TVA trace for 50 mg PMAA (powder sample). Heating rate 10°C/min
Key to traces as on p.35.

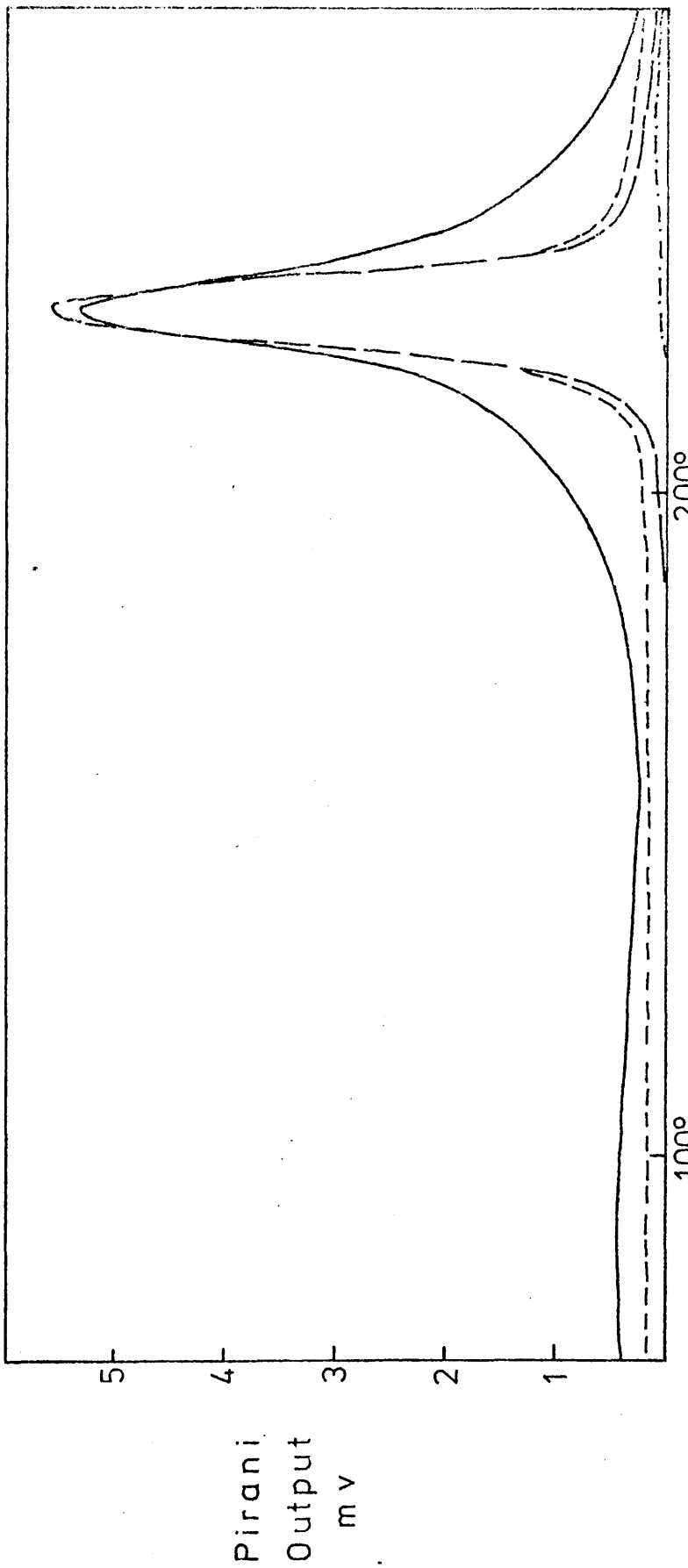


Figure (11.2). TVA trace for a 200 mg sample of PMAA up to 275°C
Heating rate 5°C/min. Powder sample.

figures (11.3) to (11.6). The character of the traces progressively changes as the MAA content of the polymers increases. In all four cases, there are two principal regions of interest; (1) the large peak with maximum around 400°C, and (2) the small peaks ranging from 100°C to the temperature of initiation of the large peak. The major trends for both these regions are discussed below ;

(1) Large peak around 400°C

As may be seen from Table (11.3), as the MAA content of the copolymers increases, both the temperature of initiation and Tmax values increase up to those for PMMA. MMA monomer production, as illustrated by the limiting rate behaviour of the -75°C trace, is apparent only for the two copolymers of lowest MMA content.

Thus stabilisation of PMMA depolymerization is apparent in all the copolymers, caused by the presence of anhydride ring structures in the chain, which inhibit depolymerization. In copolymers of high MAA content, depolymerization occurs through a small number of MMA units before being terminated by an anhydride ring structure, while in copolymers of low MAA content, depolymerization can occur through longer sequences of MMA units before being terminated.

TABLE 11.3

Temperature of initiation and Tmax for PMAA and the MMA - MAA copolymers.

Sample	T initiation	T max
MMA - MAA 1	327°C	397°C
MMA - MAA 2	343°C	407°C
MMA - MAA 3	351°C	417°C
MMA - MAA 4	370°C	443°C
PMAA	364°C	443°C

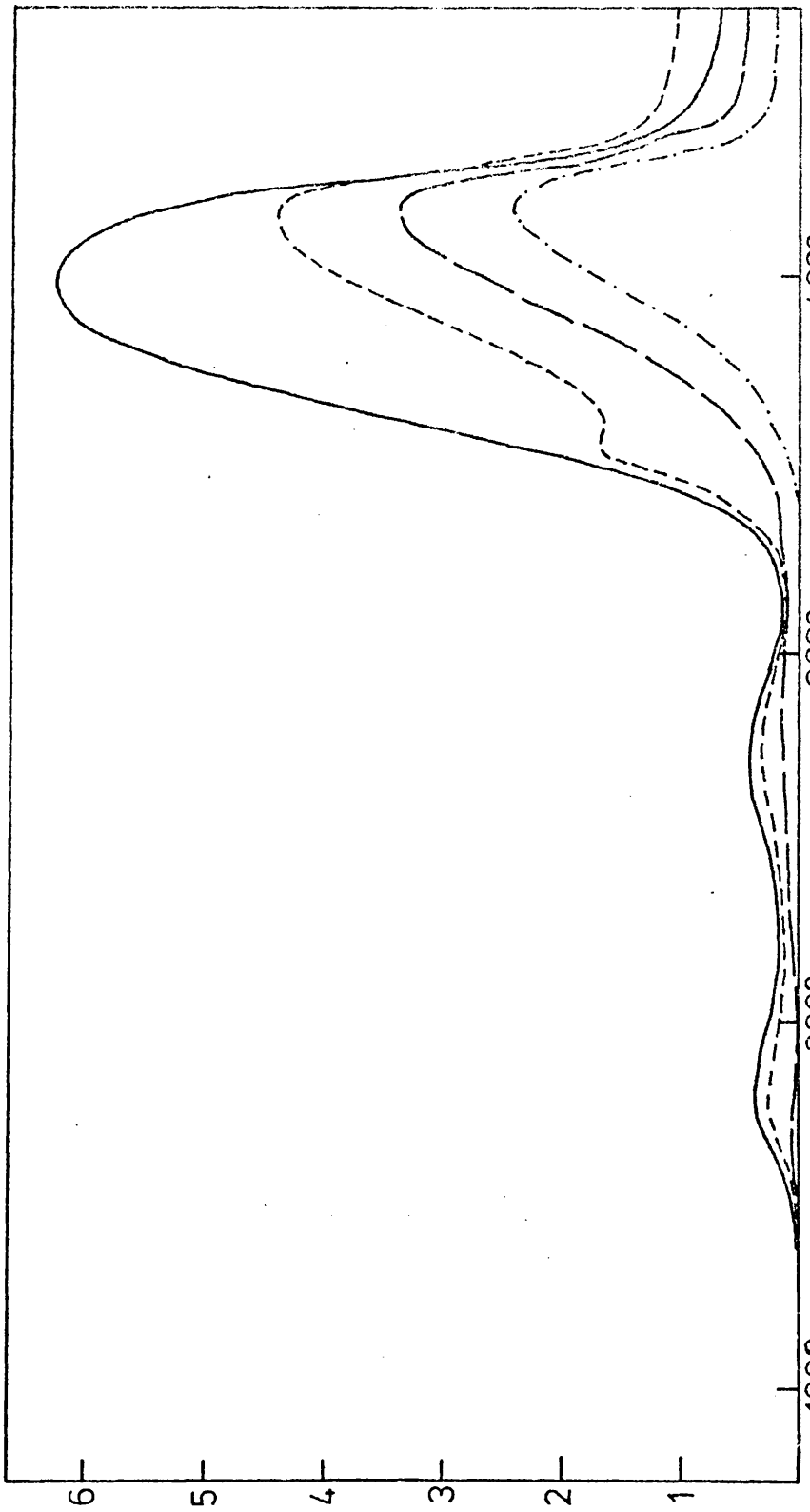


Figure (11.3). TVA trace for 50 mg of the 10% MAA - MMA copolymer (powder sample). Heating rate 10°C/min.

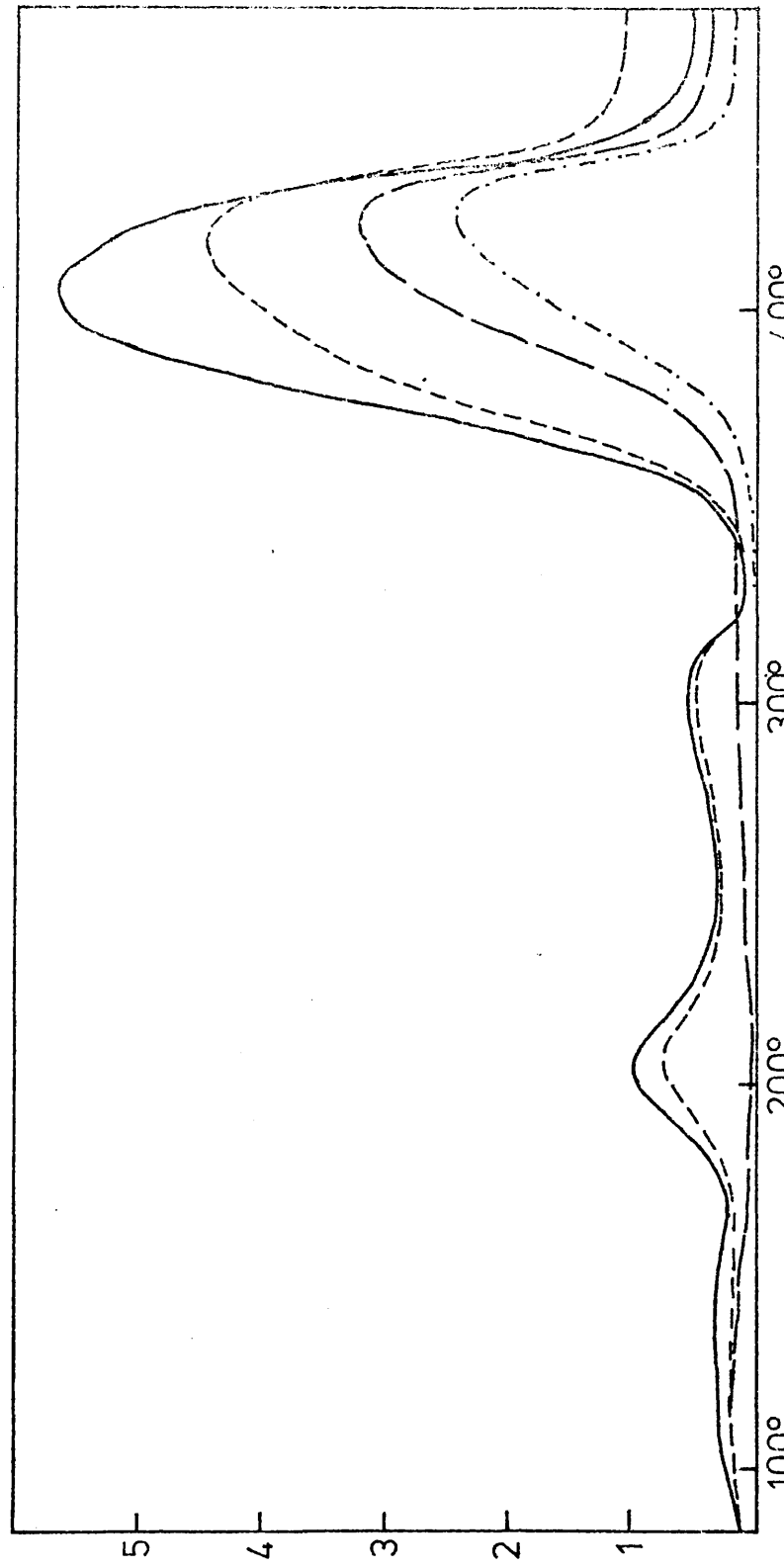


Figure (11.4). TVA trace for 50 mg of the 19% MAA – MMA copolymer (powder sample). Heating rate 10°C/min.

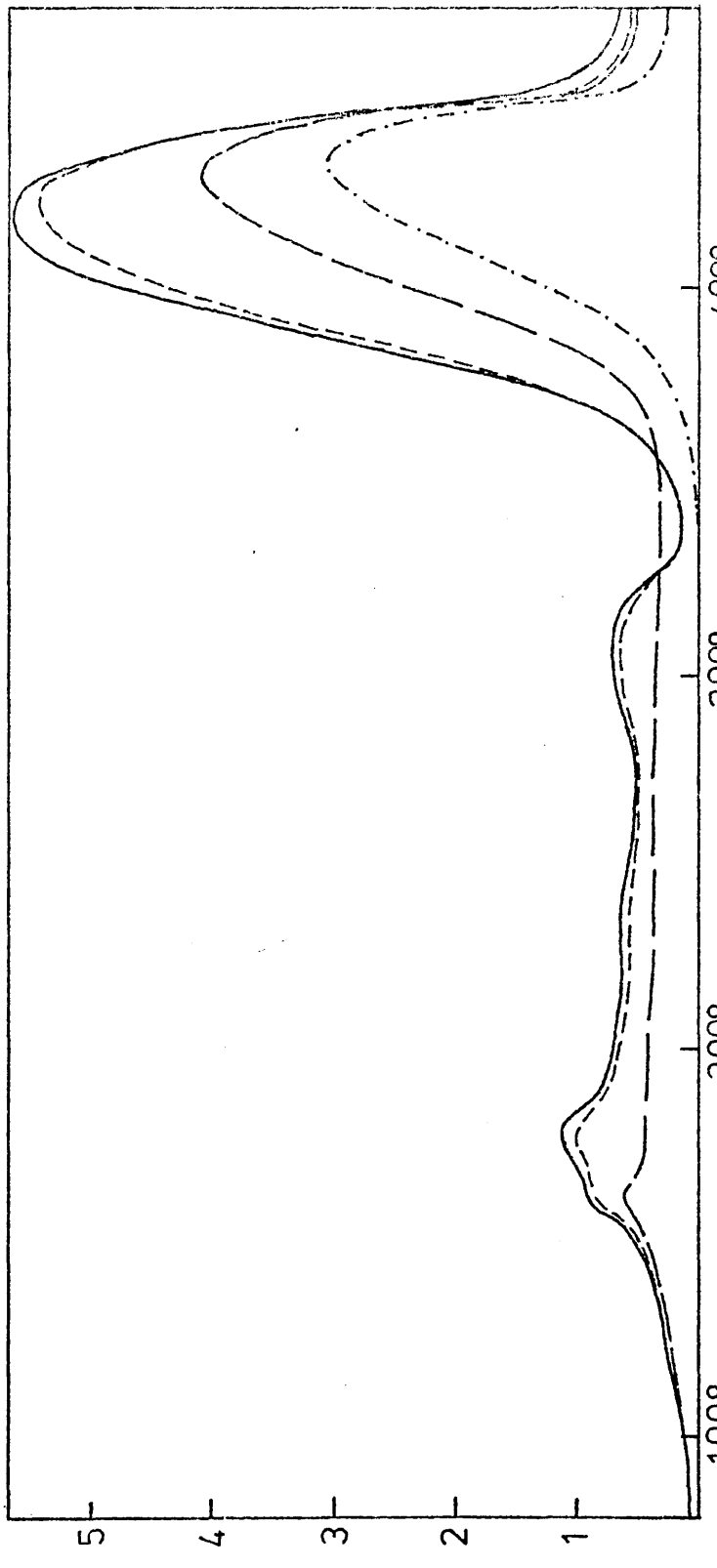


Figure (11.5). TVA trace for 50 mg of the 33% MAA - MMA copolymer (Powder sample)
Heating rate 10°C/min.

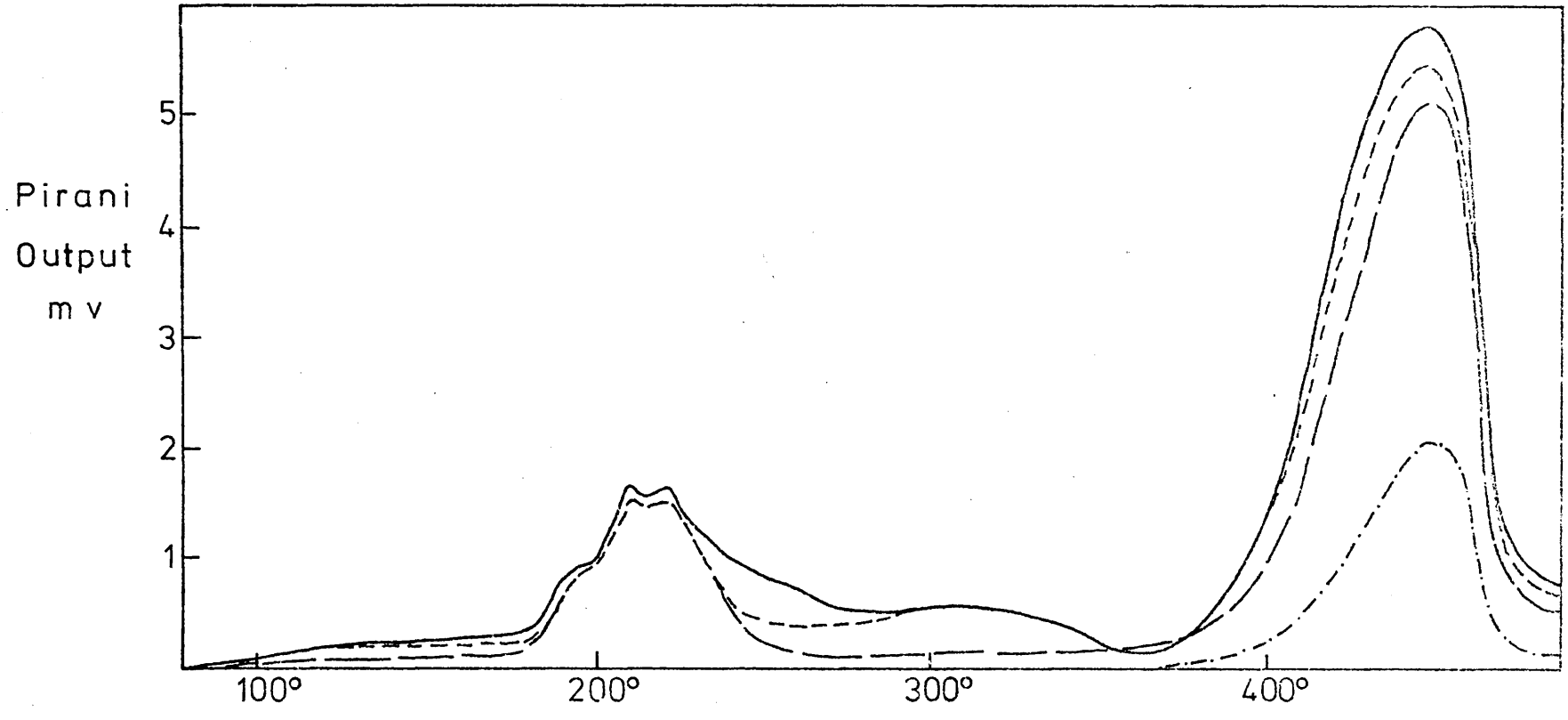
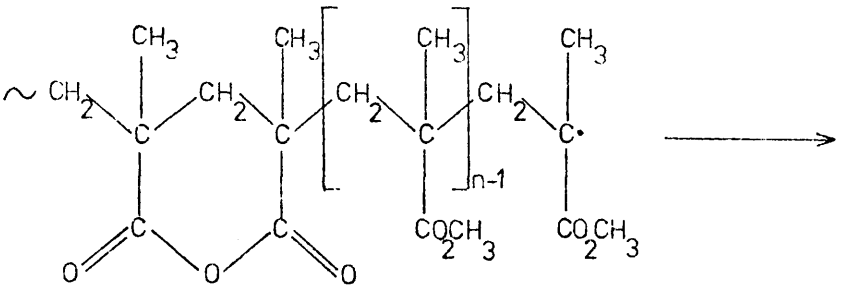
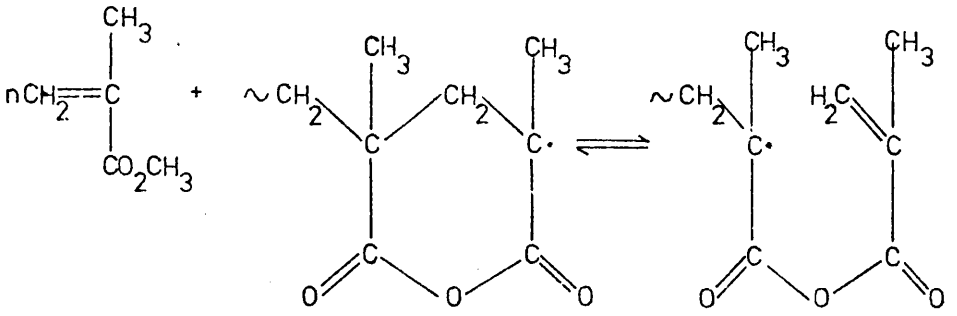


Figure (11.6). TVA trace for 50 mg of the 75% MAA - MMA copolymer (powder sample). Heating rate 10°C/min.

The inhibition is probably the result of an equilibrium set up between the anhydride radical and the radical which is the product of the liberation of one further ethylenic unit from the chain end (11). These processes are illustrated below:-





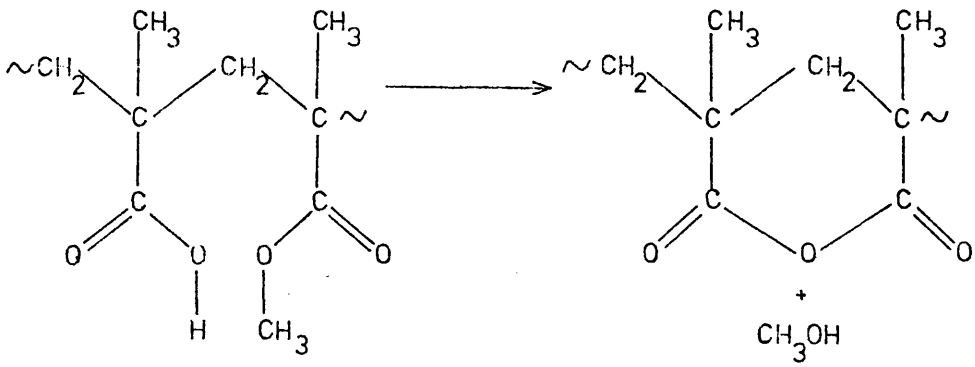
The amount of monomer obtained from each copolymer will depend on the value of n , the length of the MMA sequences in the copolymer and this will be greatest for those copolymers of highest MMA content.

(2) Small peaks at lower temperatures

For the three copolymers of highest MAA content, there is, up to approximately 200°C, evolution of absorbed water plus some of the precipitant petroleum spirit since there is deviation of the -100°C trace from the baseline, and this is consistent with the behaviour of petroleum spirit in the TVA apparatus. At about 200°C more extensive volatilization occurs for all the copolymers, and by analogy with PMAA this may be attributed to water and precipitant. Volatilization continues in the copolymers, unlike PMAA, and reaches a maximum rate around 300°C. The material volatilised (besides water)

has a limiting rate at ~100°C, and methanol, which was detected amongst the volatile products at this stage, was previously found (33) to give similar behaviour in the TVA apparatus. Figure (11.7) illustrates in more detail to (325°C), the behaviour of the two copolymers of highest MAA content, showing more clearly the effects outlined above.

This extra volatilisation is most probably due to methanol, formed by reaction between adjacent ester and acid groups and resulting in the same anhydride structure as obtained by dehydration. This reaction is analogous to the acid-catalysed esterification of an ester (91),



THERMOGRAVIMETRIC ANALYSIS

TG curves for PMMA (FR2) and PMAA are reproduced in figure (11.8). For the PMMA sample which has a fairly low molecular weight the two-stage depolymerization of PMMA is clearly illustrated by a pronounced two-stage weight loss curve which results in a residue of less than 1% at 500°C. For PMAA there are three distinct regions of weight loss; the initial 2% loss of absorbed water; the subsequent 12% weight loss of water (from the dehydration reaction) and precipitant; and the final large weight loss due to fragmentation of the residual polymer chain, leaving a residue of 6% of the original sample weight at 500°C. The theoretical maximum weight loss of water from anhydride formation

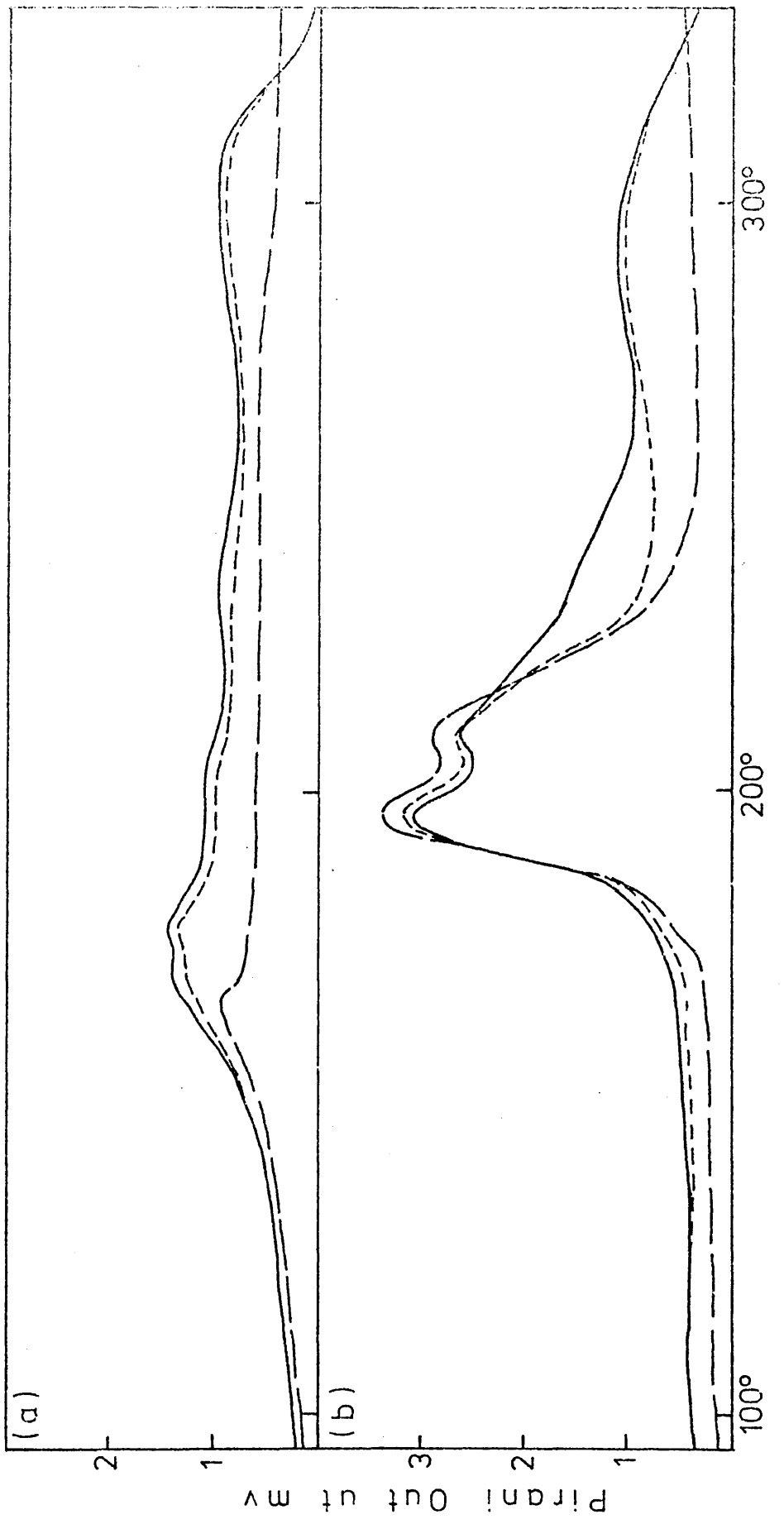


Figure (11.7). TVA traces for 200 mg samples (as powders) of ;
(a) 33% MAA-MMA, (b) 75% MAA-MMA copolymers.
Heating rate 5°C/min.

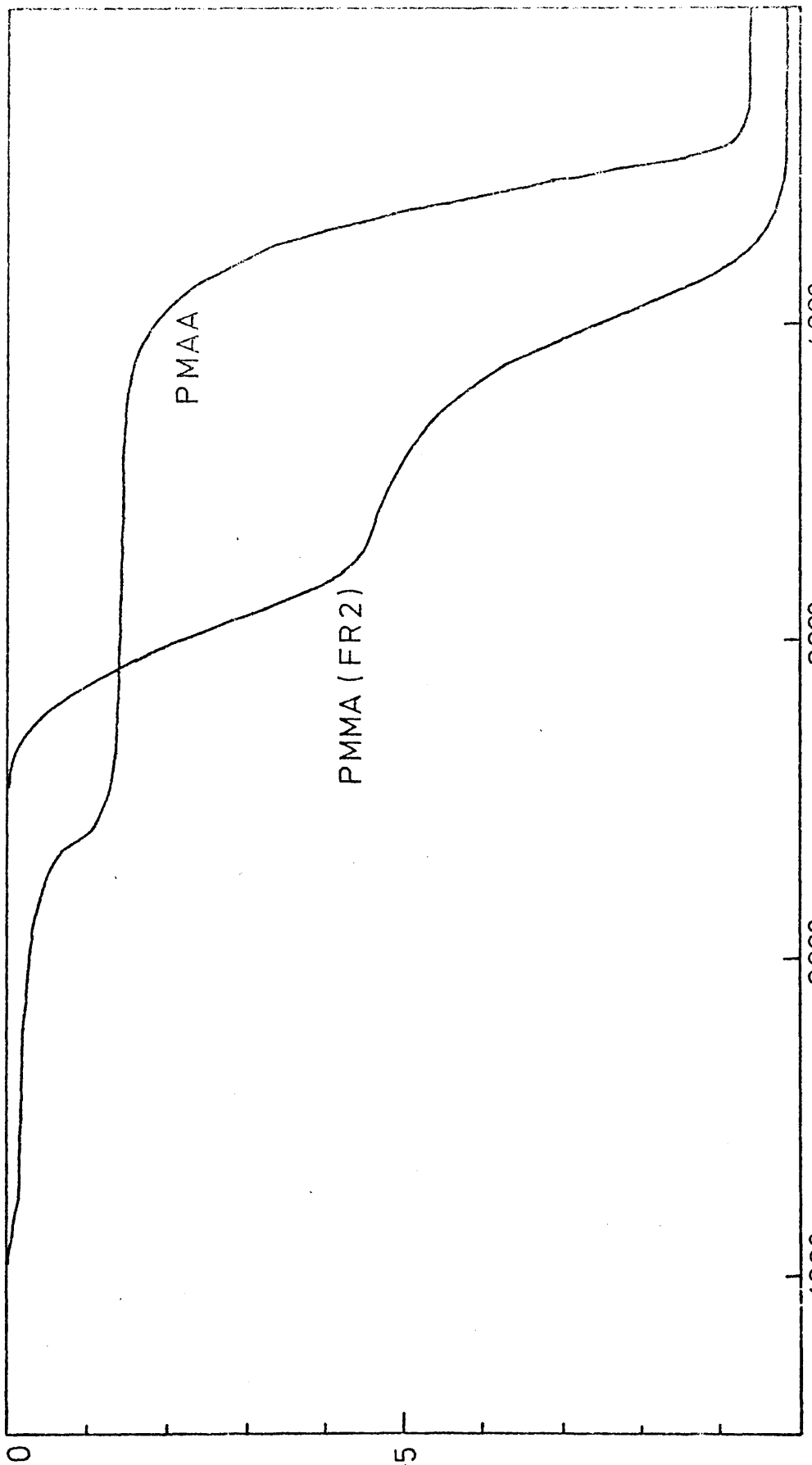


Figure (11.8). TG curves for PMAA and PMMA (FR2), degraded under N_2 at $10^{o}C$/min. 10 mg powder samples.

is 10.47% of the original sample weight, which is less than the 12% weight loss recorded. The difference may be due to precipitant and traces of methacrylic acid monomer.

Figure (11.9) shows the TG curves for the four MMA - MAA copolymers. The 10% MAA copolymer shows a 3.5% weight loss at 300°C and is more stable to weight loss than either homopolymer at this temperature. At 300°C, the 19% MAA copolymer has a weight loss of 11%, the 75% MAA copolymer a 14% weight loss, while the 33% MAA copolymer is the least stable with a 22% weight loss. This order of stability with respect to weight loss may be a reflection of the sequence distribution of the copolymers, and their facility to provide maximum interaction between adjacent acid and ester groups, which results in the elimination of methanol and hence a greater weight loss. The situation is complicated, however, by the production of methyl methacrylate monomer from the copolymers.

DIFFERENTIAL THERMAL ANALYSIS

DTA curves for PMMA (FR3), PMAA and the 75% MAA copolymer are shown in figure (11.10). PMMA has a small endotherm around 100°C which is close to the glass transition temperature of 104°C (92), and a large endotherm beginning around 300°C which is due to depolymerization to monomer. PMAA has an endotherm around 100°C associated with the loss of absorbed water; the complex endothermic system beginning at 200°C corresponds to loss of water by dehydration and also evolution of the precipitant. Above 400°C the curve is complex during fragmentation of the residual anhydropolymethacrylic acid chain.

The 75% MAA copolymer, as with the other copolymers has no endotherm between 300° and 400°C, showing inhibition of depolymerization of MMA units. However, the regions around 200°C and above 400°C are similar to those for PMAA. It is an interesting feature of PMAA (15), and the copolymers, that they sinter at the temperature

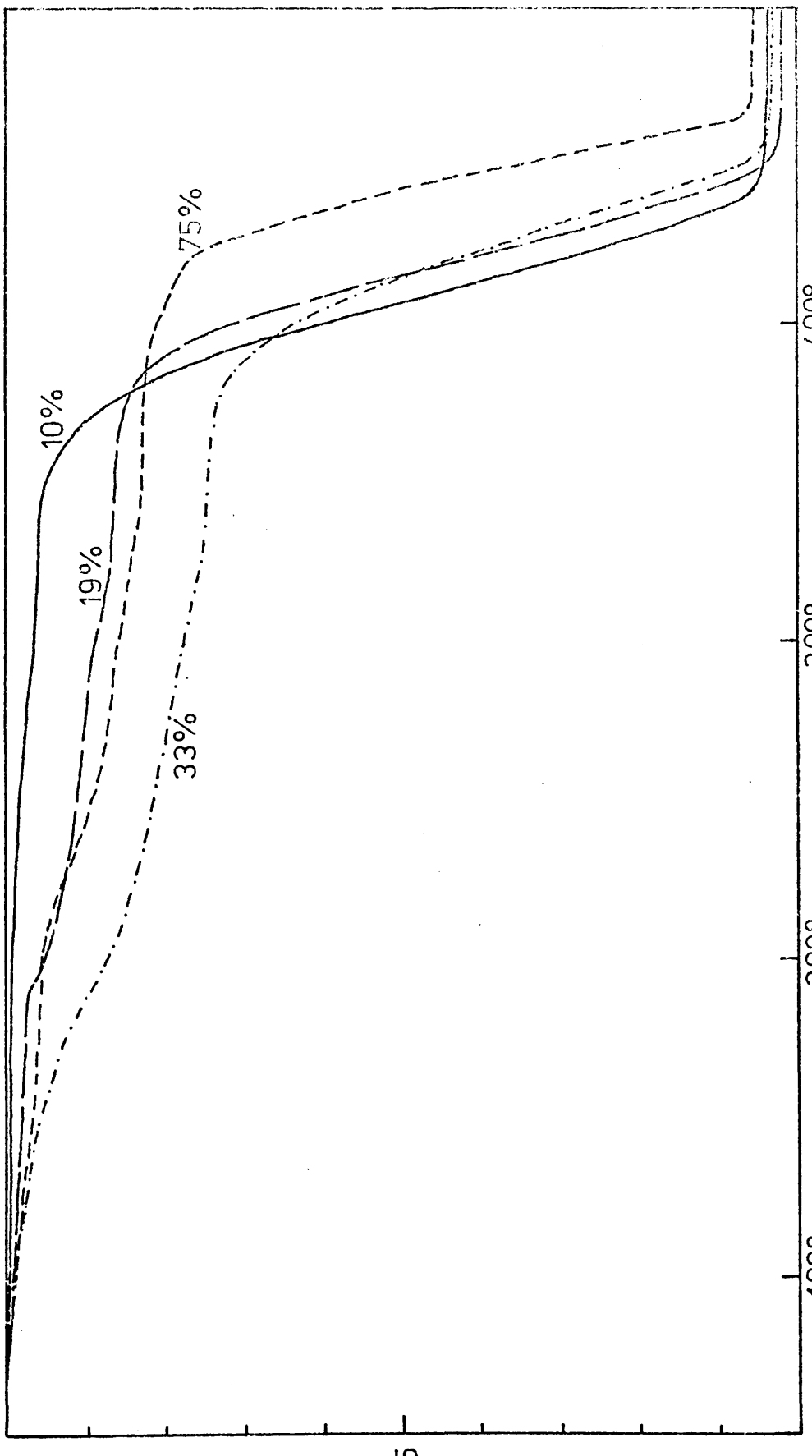


Figure (11.9). TG curves for the MAA-MMA copolymers, degraded under N_2 at 10°C/min.
10 mg powder samples.

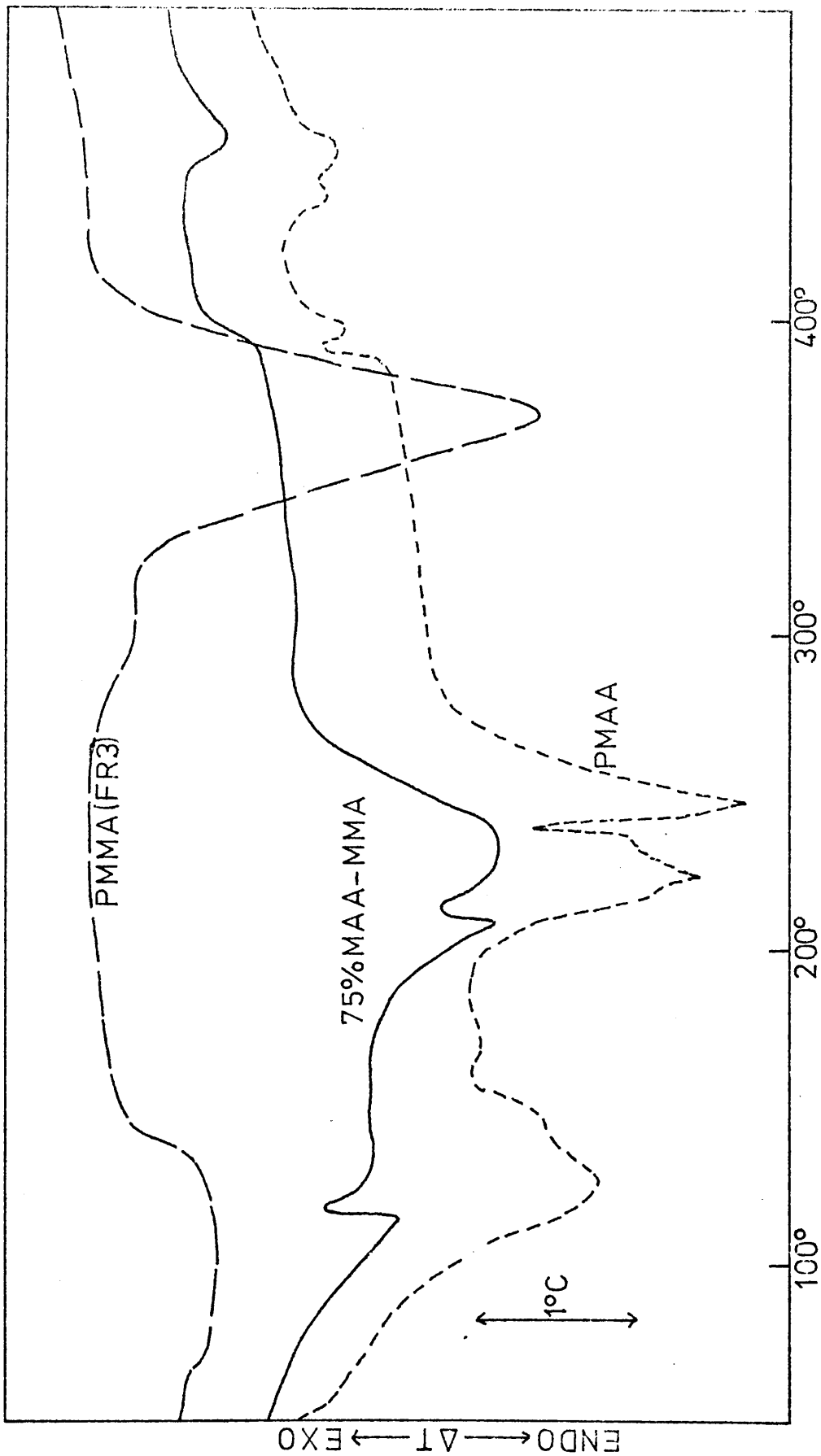


Figure (11.10). DTA traces for PMMA (FR3), PMAA and the 75% MAA - MMA copolymer at 10°C/min, under N_2. 10 mg powder samples.

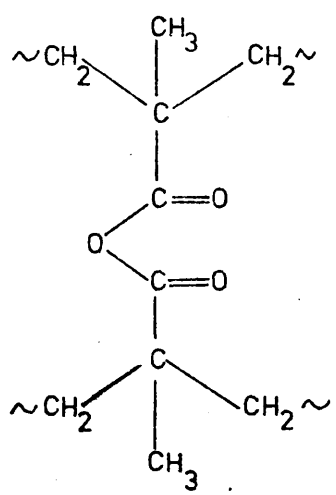
of anhydride formation and subsequently undergo degradation and fragmentation before melting.

RESIDUE ANALYSIS

Infra-red spectra of the 19% MAA copolymer, and the product obtained after partial degradation at 5°C/min to 320°C, are shown in figure (11.11). It can be seen that this treatment has removed the broad "bonded" O-H absorption (3700-2800 cm^{-1}), and the shoulders on the carboxyl absorption at 1700 and 1680 cm^{-1} due to the MAA units in the copolymer. New bands appear at 1800 and 1758 cm^{-1}, in close agreement with the twin peaks obtained by Grant and Grassie (15) for anhydropolymethacrylic acid (1795 and 1750 cm^{-1}), and also with the values obtained (93) for the corresponding six-membered ring glutaric anhydride (1802 and 1765 cm^{-1}). The peak at 1012 cm^{-1} in the spectrum of the degraded copolymer corresponds to the intense C - O - C absorption (1022 cm^{-1}) of degraded PMAA.

INSOLUBILITY OF RESIDUE.

Heating the copolymers to 340°C at 5°C/min produced residues, light yellow in colour, which were insoluble in common organic solvents (e.g. chloroform, absolute alcohol, dimethyl formamide, benzene, etc). Degraded PMAA was also found to be insoluble (15) and it was suggested that this was caused by the presence of a few cross-links of the isobutyric type,



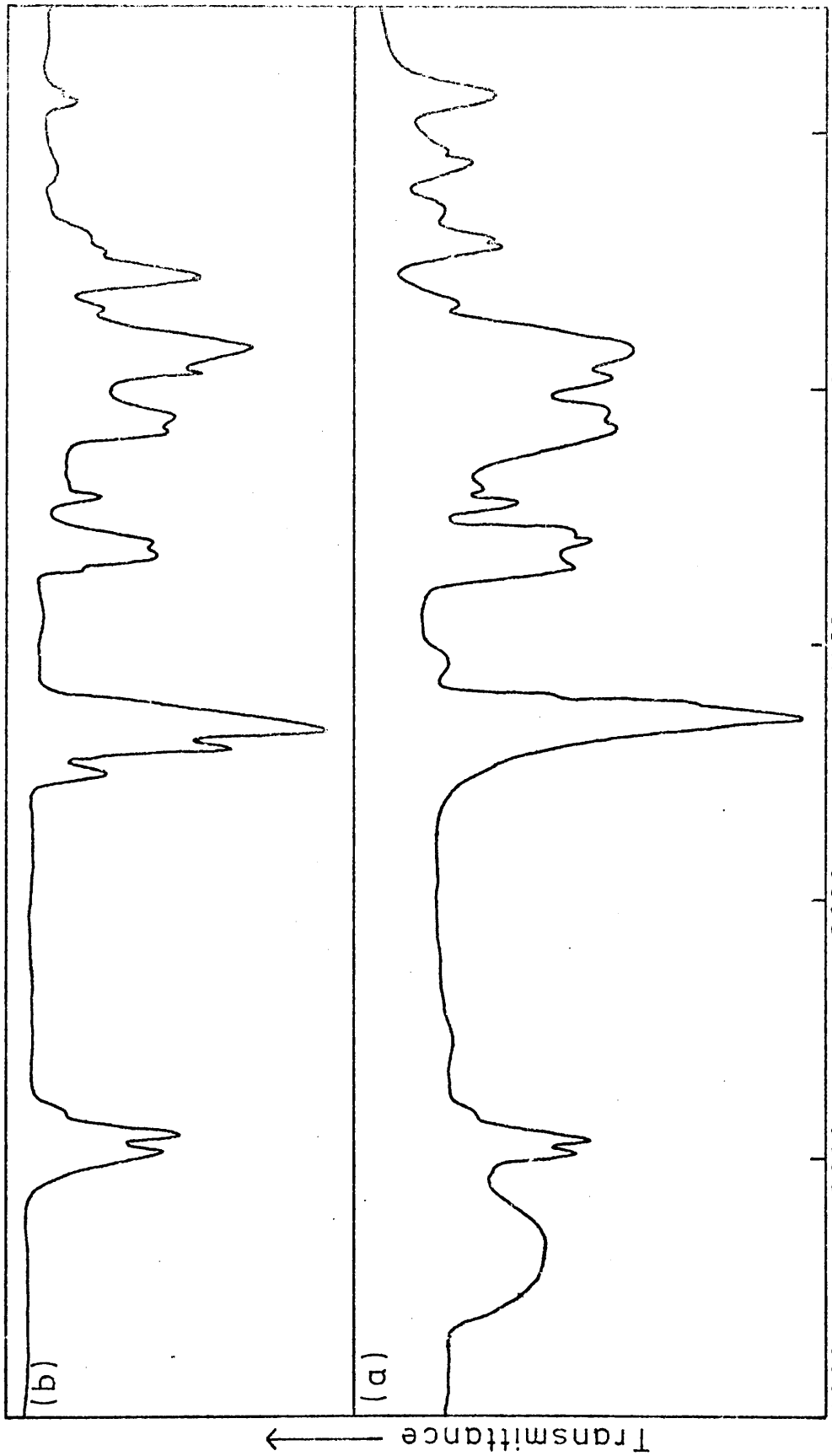
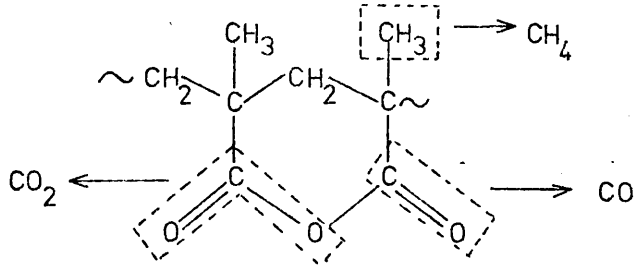


Figure (11.11). Infra-red spectra of (a) 19% MAA-MMA copolymer;
(b) 19% MAA-MMA copolymer degraded at 5°C/min to 320°C.

VOLATILES ANALYSIS.

(a) PMAA :- A 200 mg powder sample of PMAA was degraded at 5°C/min to 500°C, and the products obtained up to 300°C were examined separately from those obtained between 300° and 500°C. The former consisted mostly of water with a trace of MAA (observed by examination of a dried CCl_4 solution of the liquid products using infra red spectroscopy). The gaseous products from degradation between 300° and 500°C were found, by infra-red spectroscopy, to consist of CO_2, CO and CH_4, which probably arise from fragmentation of the anhydride ring structures (34).



(b) MMA - MAA Copolymers :- 200 mg powder samples were degraded isothermally under vacuum at 300°C for two hours, and infra-red spectra of the gaseous products and of a dried CCl_4 solution of the liquid products obtained. The gaseous spectrum showed minor quantities of MMA and CO_2, but the main product was methanol. The liquid, which was dried to remove water and which was detectably acid from MAA monomer, contained methanol as a major product and both monomers as minor products. These observations were confirmed by mass spectrometry. The highly volatile products of the higher temperature degradation (300° to 500°C) carried out in a closed system were CO, CO_2 and CH_4, and probably arose from a fragmentation process similar to that described for PMAA.

Quantitative analysis of the major liquid products, H_2O, methanol and MMA monomer was carried out by GLC, to determine the extent of each of the major reactions; viz, anhydride formation, by

loss of water between adjacent carboxylic acid groups and by loss of methanol between adjacent acid and ester groups; and depolymerization to yield MMA monomer. Measurements were carried out on the Perkin-Elmer F11 Gas Chromatograph at 60°C, using a column containing 13½% MEA and 6½% Di-2-Ethyl Hexyl Sebacate on Chromosorb, with n-propanol as internal standard. The sensitivities of the products compared to the standard were measured, as before, using the method of cut-outs to determine peak areas. Analyses were made of products obtained by degrading 100 mg powder samples to 500°C at 10°C/min. under vacuum.

A typical chromatogram for products from the 19% MAA copolymer is reproduced in figure (11.12) and the peaks for MMA, water, methanol and the standard are indicated. The sharp peaks at the beginning of the trace are due to dissolved gases (CO_2 etc) and to the precipitant petroleum ether. The amount of product obtained (in mg), from degradation of 100 mg of each copolymer is shown in Table (11.4). The principal features of these results, as the percentage of MAA in the copolymer increases, are :-

(1) the quantity of water obtained increases,

(2) the quantity of MMA monomer obtained decreases,

(3) the quantity of methanol obtained increases up to the 75% copolymer at which stage there is a decrease, probably due to competition from water formation.

ANALYSIS OF THE COLD RING FRACTION.

Infra-red spectra of the dark brown cold ring fractions obtained from PMAA and the copolymers between 300° and 500°C were run in CCl_4 solution, and the region of interest (for PMAA and the 75% MAA copolymer) is shown in figure (11.13). For PMAA, the peaks at 1806 and 1765 cm^{-1} are due to the anhydride ring structures, and the peak at 1703 cm^{-1} indicates some residual acid groups. For the 75%

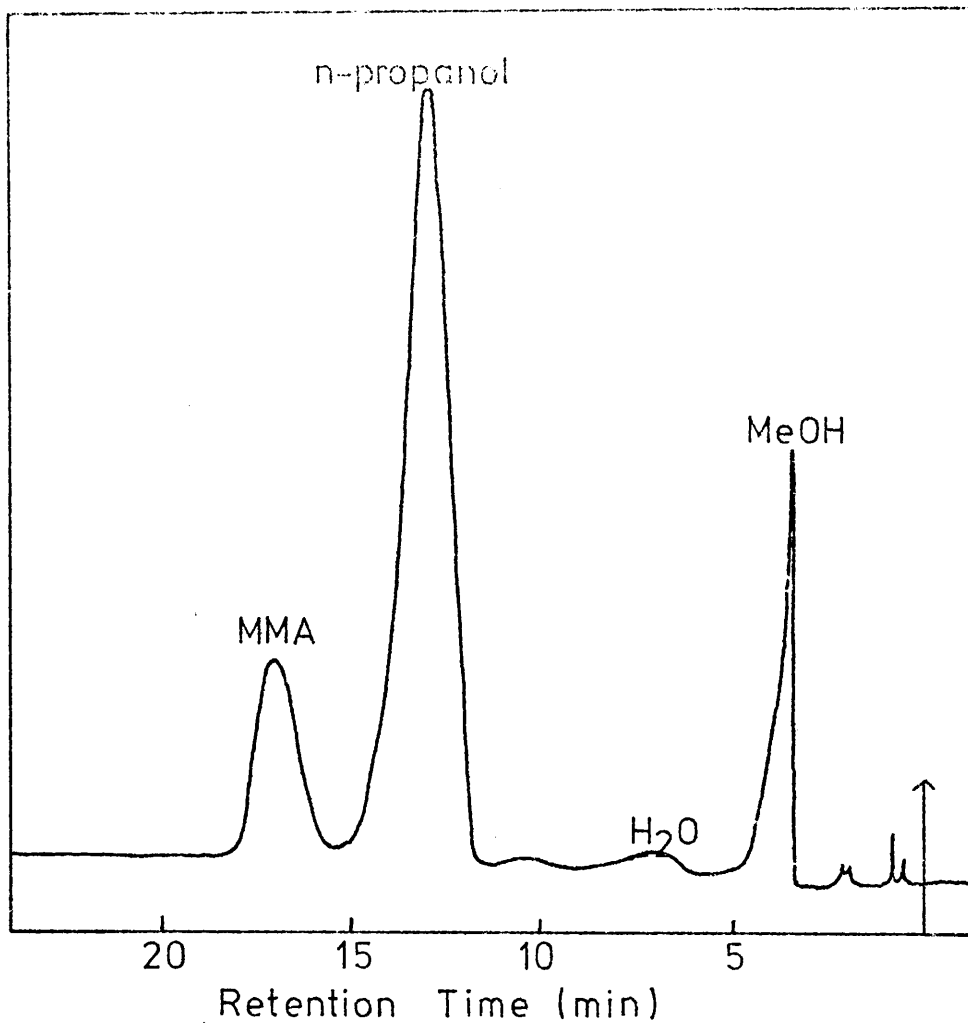


Figure (11.12). GLC trace for the products of degradation at 10°C/min to 500°C, from 100 mg of the 19% MAA-MMA copolymer.

TABLE (11.4)

Quantitative analysis (by GLC) of the production of water, methanol and MMA monomer from degradation of 100 mg of the MAA-MMA copolymers at 10°C/min to 500°C.

Product (mg)	MAA - MMA Copolymer			
	10%	19%	33%	75%
H_2O	Trace	0.83	4.50	6.80
MeOH	7.95	9.20	11.30	7.73
MMA	56.10	38.30	25.10	4.23

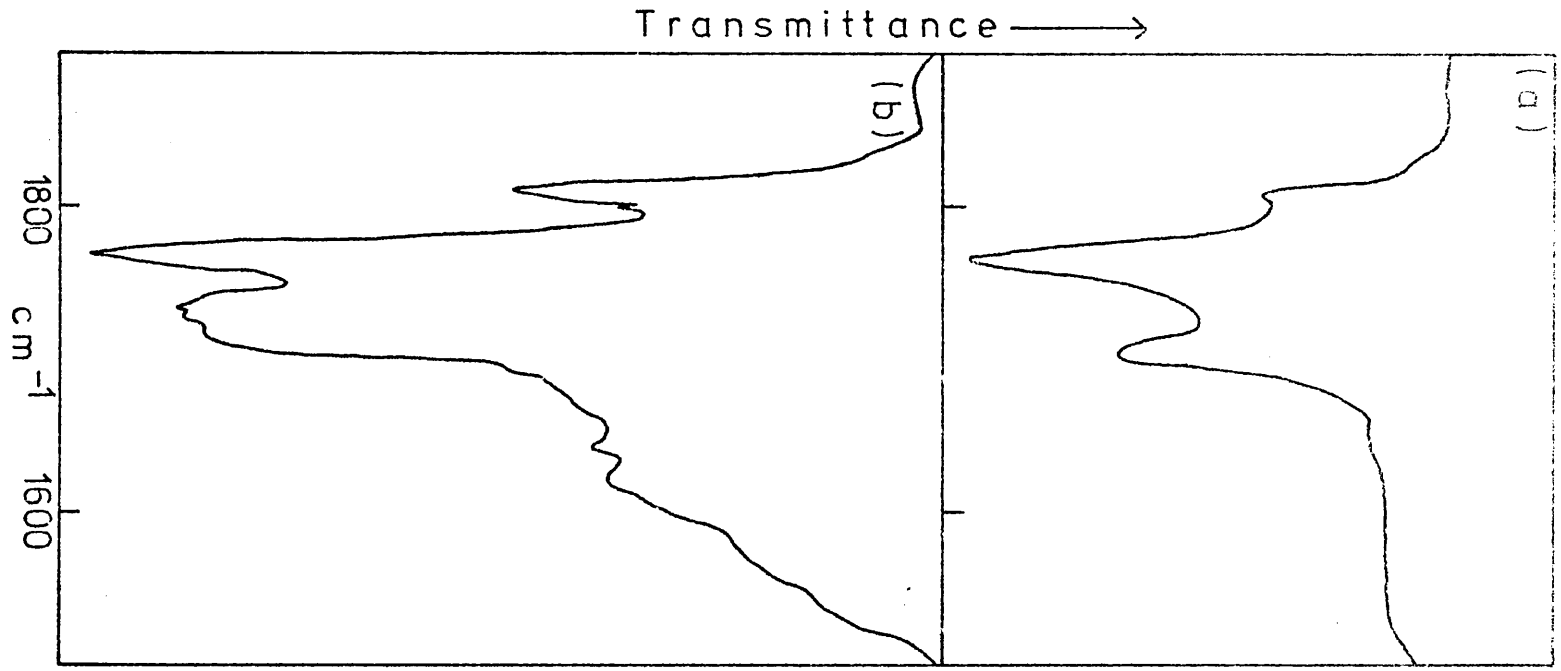
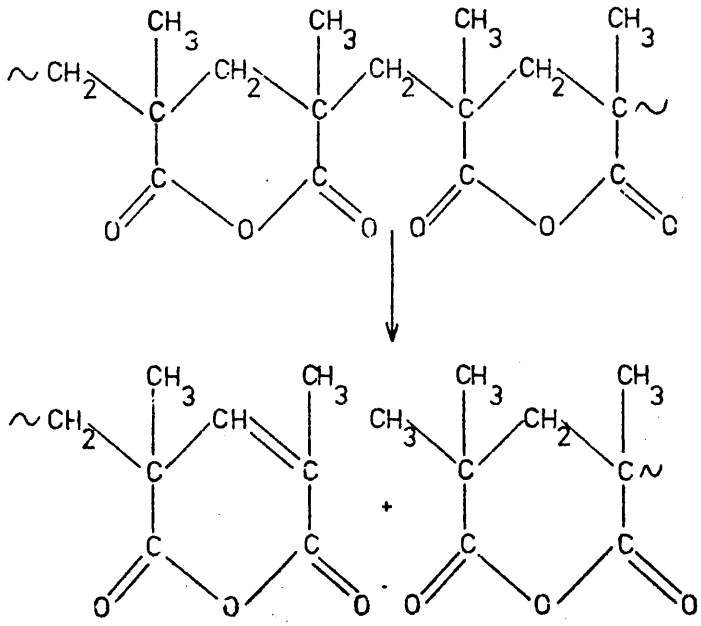


Figure (11.13). Infra-red spectra of the region of interest of (a) CRF of PMAA; (b) CRF of the 75% MAA-MMA copolymer. Spectra obtained in CCl_4 solution.

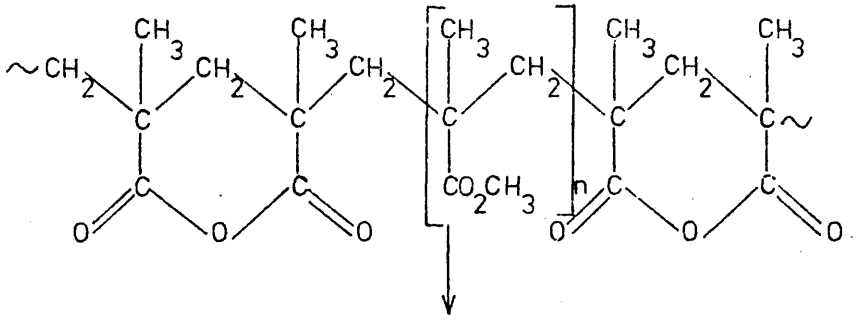
copolymer, the spectrum has similar features to that described for PMAA, as well as a large peak at 1730 cm^{-1} for residual methacrylate ester groups. The peaks for the anhydride structures occur at 1810 and 1770 cm^{-1} and there is a shoulder for acid groups around 1700 cm^{-1}. Between 1600 and 1700 cm^{-1} there is a broad absorption band which may indicate the presence of some unsaturation in the structures. This is not inconsistent with possible structures of the cold ring fraction, which will be outlined below.

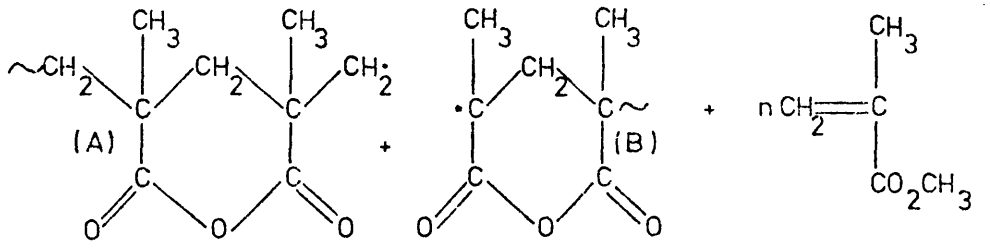
The formation of the cold ring fraction roughly parallels the production of the non-condensable volatiles in both PMAA and the copolymers, indicating perhaps that chain scission follows the elimination of these products from the anhydride ring structures. However, another site of chain scission may be the bridging methylene group between the anhydride rings, a situation analogous to that observed (35) during the decomposition of poly (methyl vinyl ketone) and poly (methyl isopropenyl ketone). Breaking of the bond between the methylene group and the adjacent ring structure, possibly accompanied by hydrogen transfer, could leak to the formation of chain fragments without concurrent production of highly volatile material:



The ultraviolet spectrum of the cold ring fraction has an absorption maximum at 212 mμ which is consistent with values for unsaturated anhydrides (94), suggesting that the above reaction is a possible pathway for the formation of chain fragments in PMAA and the MAA copolymers.

For the copolymers, a further possible reaction route exists for the formation of the cold ring fraction, viz, chain scission at residual MMA units and subsequent depolymerization to yield structures identical to those above.

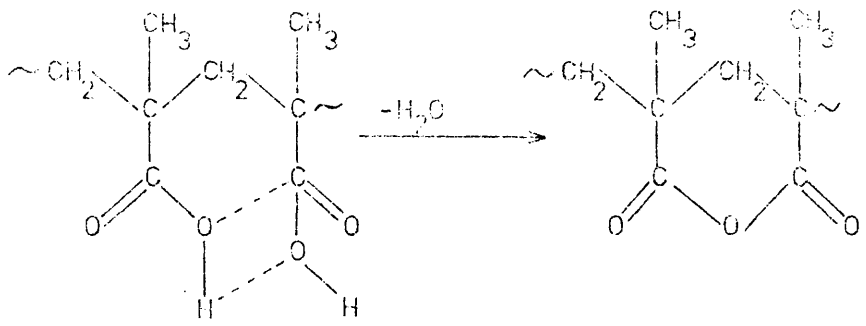




(A) and (B) can undergo hydrogen transfer to give a saturated and unsaturated anhydridi species, as before.

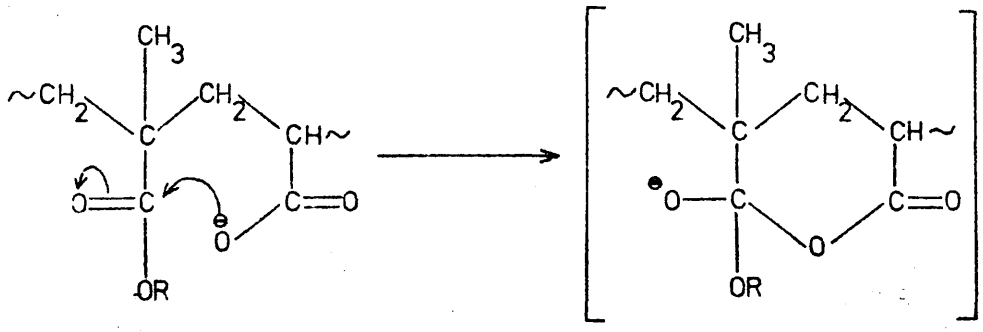
MECHANISM OF ANHYDRIDE FORMATION

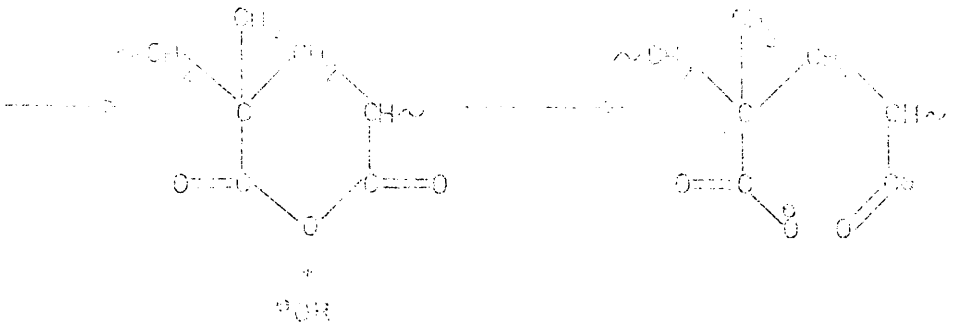
Grant and Grassie (15) proposed that the mechanism of anhydride formation in PMAA is analogous to an acid catalysed esterification of a carboxylic acid with an alcohol (91). The overall reaction is represented as passing through the transition state,



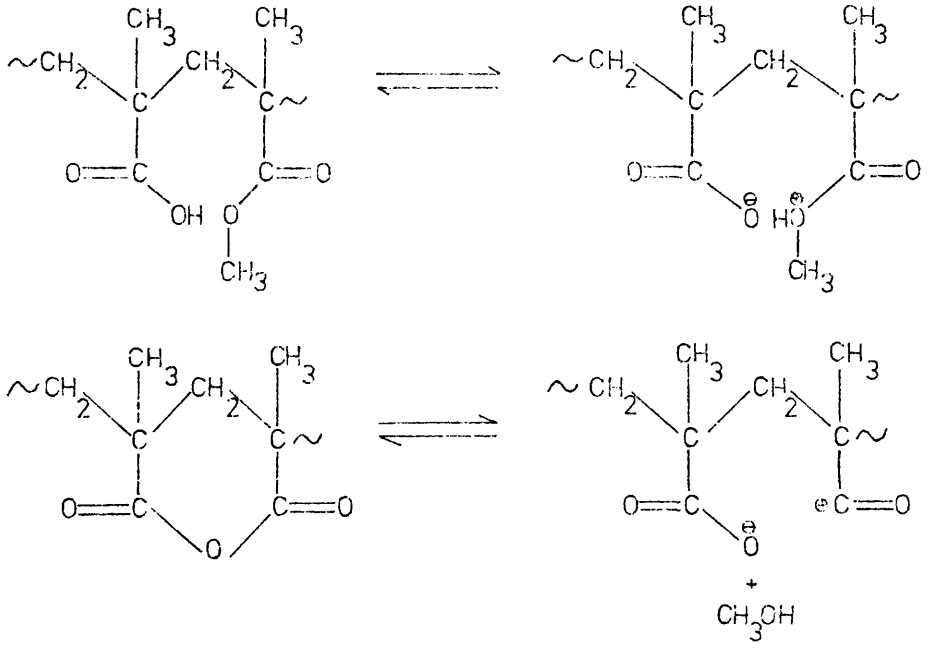
It was also suggested (15) that a steric effect is responsible for the ease of formation of anhydropolymethacrylic acid, compared to the model glutaric anhydride which requires a temperature of 300°C for formation. This steric effect involves adjacent acid groups in the chain being fairly close together, a conformation geometrically favourable for this reaction.

In essence this is an example of neighbouring group participation, an effect which is manifested in many chemical reactions of polymers, such as the hydrolysis of an (acrylic acid) - acrylamide copolymer (95) which proceeds as a two-stage reaction, the first of which is 50 to 100 times faster than the second, and results from an interaction between an amide and a neighbouring acid group: the second, slow step corresponds to hydrolysis of amide groups by external acid. Also the rate of solvolysis of methacrylate esters is increased by many orders of magnitude compared with a monocarboxylic ester, if there exists a neighbouring carboxyl group. The ester hydrolysis is due to the attack of an adjacent carboxyl on the carbonyl carbon of the ester group, the first product of the reaction being an acid anhydride (96),

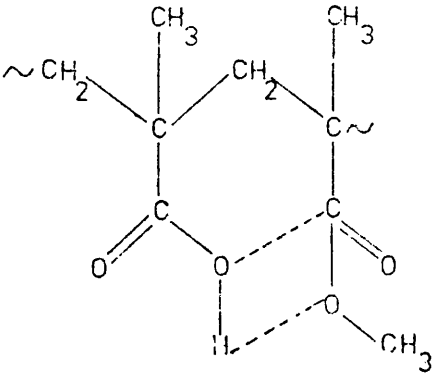




A similar situation exists in the MMA - MAA copolymers, and the production of methanol, with concurrent formation of an anhydride ring, may arise by a reaction analogous to the acid catalysed esterification of an ester (91);



Once again, the overall reaction may be represented as passing through the transition state;



Examination of molecular models shows that a conformation in which adjacent acid and ester groups are fairly close together, is at least no more strained than any other, and might well be the preferred conformation over considerable segments of the polymer chain.

A brief examination of (acrylic acid) (methyl methacrylate) copolymers revealed many similar features. TVA showed inhibition of depolymerization of the MMA units, infra-red spectroscopy indicated the formation of six-membered ring anhydride rings in the residue, and methanol was detected amongst the volatile products.

SUMMARY.

Like PMAA, copolymers of MMA and MAA undergo dehydration between pairs of carboxylic acid groups to form six-membered ring anhydrides. The copolymers however, also form these cyclic anhydrides by elimination of methanol between adjacent acid and ester groups. The presence of these anhydride rings in the polymer chain enhances the thermal stability of the copolymers by inhibiting depolymerization of the MMA units.

APPENDIX ONE

Absorption Frequencies for Methyl Acetate and Methyl Methacrylate in the Gaseous Phase, with Relative Intensities - See Chapter Three.

Methyl Methacrylate		Methyl Acetate	
Wavelength	Rel. Intensity	Wavelength	Rel. Intensity
3580	1	3545	1
3470	1	3008,3000,2995 (t)	2
3110	1	2850	1
2998	3	2080	1
2960	4	1895	1
2850	2	1775	9
1750,1740 (d)	9	1760	9
1650,1640 (d)	2	1650	1
1460,1450,1440 (t)	4	1441	4
1330,1310 (d)	6	1370	5
1200,1160 (d)	10	1245	10
1030,1020 (d)	2	1047	5
940	5	980	2
825,815 (d)	3	843	3

APPENDIX TWO

1. Data for estimation of acetic acid and HCl from PVA (BDH), PVC Breon 113 and a 1:1 mixture by weight of these polymers degraded under vacuum at 220°C. See figure (4.9), chapter four.

PVC BREON 113

Time (min)	50	100	150	200	250	300	350
ml $^{N}/_{100}$ NaOH	7.49	13.75	19.10	23.50	27.80	30.20	32.60
% Dehydrochlorination	9.3	17.2	23.6	29.4	34.8	37.8	40.8

PVA (BDH)

Time (min)	60	120	175	240	310	365	425	477
ml $^{N}/_{100}$ NaOH	0.35	0.66	1.11	1.43	1.83	2.13	2.46	2.86
% Deacetylation	0.60	1.13	1.90	2.45	3.14	3.66	4.22	4.90

PVA - PVC Mixture

Time (min)	40	70	100	130	160	210	290	365	420
ml $^{N}/_{100}$ NaOH (for HCl)	11.64	21.04	26.30	29.15	31.16	33.21	34.95	36.36	37.37
% Dehydrochlorination	14.6	26.3	32.9	36.4	38.9	41.5	43.7	45.5	46.2
ml $^{N}/_{100}$ NaOH (for Acetic Acid)	5.34	9.22	11.07	12.42	12.97	13.46	14.56	15.23	15.78
% Deacetylation	9.2	15.4	19.1	21.4	22.4	23.2	25.1	26.2	27.2

2. Data for estimation of acetic acid and HCl from PVA (BDH), PVC RA and a 1:1 mixture by weight of these polymers degraded under vacuum at 220°C. See figure (4.10), chapter four.

PVC RA

Time (min)	50	100	150	200	250	300
ml $^{N}/_{100}$ NaOH	8.80	16.42	23.13	28.00	31.98	35.69
% Dehydrochlorination	11.0	20.5	28.9	35.0	40.0	44.6

PVA (BDH) - As before

PVA-PVC Mixture

Time (min)	30	60	90	140	210	290	370
ml $^{N}/_{100}$ NaOH (HCl)	10.30	25.5	34.0	40.3	45.0	47.0	48.0
% Dehydrochlorination	12.8	31.9	42.5	50.3	56.3	58.8	60.0
ml $^{N}/_{100}$ NaOH (Acetic Acid)	5.45	7.9	8.5	10.5	12.6	15.5	18.3
% Deacetylation	8.8	13.6	14.7	18.0	21.7	25.7	31.5

3. Production of acetic acid from PVA (BDH) at 265°C, under vacuum, and in the presence of HCl. See figure (4.12), chapter four.

Vacuum

Time (min)	60	120	180
% Deacetylation	8.52	18.49	33.25

HCl Atmosphere.

Time (min)	15	30	45	60
% Deacetylation	14.90	45.16	76.30	94.80

4. UV absorption at 450 m μ versus % deacetylation for PVA (BDH) degraded at 265°C in vacuum and in an atmosphere of HCl.

	Vacuum							H Cl			
% Deacetylation	9.39	21.30	29.10	34.70	55.70	82.20	95.30	14.90	45.16	76.30	100.00
Absorption	.018	.020	.048	.068	.290	.204	.216	.150	.314	.420	.420

APPENDIX THREE

Estimation of acetic acid, methyl methacrylate, and methyl acetate by G.L.C. from degradation of the 30% VA - MMA copolymer at 250°C. See figure (6.9).

Time of Degradation (Hours)	% Degradation	(1) Methyl Acetate	(1) MMA	(1) Acetic Acid
1.0	6.0	2.10×10^{-2}	7.88×10^{-3}	2.99×10^{-1}
1.5	9.0	3.84×10^{-2}	8.60×10^{-3}	3.91×10^{-1}
2.0	11.4	6.20×10^{-2}	48.00×10^{-3}	5.41×10^{-1}
3.0	14.8	14.40×10^{-2}	106.00×10^{-3}	10.40×10^{-1}

(1) Quantities of products in m. moles per g of polymer.

APPENDIX FOUR

1. Isothermal weight loss data for PVA (BDH). See figure (7.1).

245°C	Time (min)	25	50	75	100	125	150	175	200
	% Wt. Loss	1.27	2.16	3.12	3.94	5.24	6.13	7.24	8.10
262°C	Time (min)	25	50	75	100	125	150	175	200
	% Wt. Loss	1.98	3.97	6.37	8.99	11.87	14.67	17.70	20.60
272°C	Time (min)	10	20	30	40	50	60	70	80	90
	% Wt. Loss	1.33	2.90	4.75	6.73	8.83	11.12	13.39	15.77	18.10
284°C	Time (min)	5	10	15	20	25	30	35	40	45
	% Wt. Loss	1.53	3.38	5.45	7.74	10.18	12.77	15.32	17.82	20.37
288°C	Time (min)	5	10	15	20	25	30	35		
	% Wt. Loss	2.18	5.15	8.36	12.23	15.90	19.79	23.47		

2. Initial rate of weight loss data for PVA (BDH). See figure (7.2).

Temp. °K	561	557	545	535	518
Initial Rate (% Wt.Loss/min) x 10	7.27	4.76	2.21	1.10	0.45

APPENDIX FIVE

1. Isothermal weight loss data for PVF (III). See figure (8.3)

238°C	Time (min)	25	50	75	100	125	150	175	200			
	% Wt.loss	2.13	3.44	4.78	6.05	7.55	9.05	10.24	11.47			
244°C	Time (min)	25	50	75	100	125	150	175	200			
	% Wt.loss	2.35	4.39	6.31	8.27	10.28	12.29	14.39	16.39			
251°C	Time (min)	10	20	30	40	50	60	70	80	90	100	110
	% Wt.loss	1.62	3.64	5.58	7.44	9.21	11.04	12.34	13.98	15.49	17.10	18.40
260°C	Time (min)	5	10	15	20	25	30	35	40	45	50	
	% Wt.loss	1.15	2.98	4.84	6.59	8.30	10.00	11.74	13.81	14.83	16.39	
269°C	Time (min)	5	10	15	20	25	30	35				
	% Wt.loss	2.59	5.22	7.81	10.51	13.00	15.56	17.93				
282°C	Time (min)	3	6	9	12	14						
	% Wt.loss	2.31	5.81	9.79	17.86	20.03						

2. Initial rate of weight loss data for PVF (III). See figure (8.4).

T°K	555	542	533	524	517	511
Initial Rate (% Wt.Loss/Min)	1.35	0.51	0.33	0.17	0.08	0.05

APPENDIX SIX

1. Weight of products (acetic acid and MMA monomer) evolved from degradation of unmixed and mixed 1:1 by weight mixtures of AgAc and PMMA (100 mg of each compound). Temperature of degradation 207°C. See figure (10.7).

UNMIXED	Time (min)	21	40	62	85	125
	Weight (mg)	4.1	13.7	17.6	25.4	25.4
	% Weight Loss	2.1	6.9	8.8	12.7	12.7
MIXED	Time (min)	20	40	61	80	100
	Weight (mg)	9.9	33.9	43.9	51.2	53.5
	% Weight Loss	5.0	17.0	22.0	25.6	26.8

2. Weight of acetic acid and MMA monomer evolved from degradation of unmixed and mixed 1:1 by weight mixtures of AgAc and PMMA (100 mg of each compound). Temperature of degradation 207°C.

UNMIXED	Time (min)	21	40	62	85	125
	Weight MMA(mg)	3.6	10.0	13.5	17.6	17.6
	" Acetic Acid (mg)	0.5	3.7	4.1	7.8	7.8
MIXED	Time (min)	20	40	61	80	100
	Weight MMA(mg)	9.5	29.1	38.6	42.6	43.5
	" Acetic Acid (mg)	0.4	4.8	5.3	8.6	10.0

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